Study of Catalyst Support Effect with Nickel Promoter in Thermocatalytic Decomposition of Methane for Hydrogen Production

by

Syazana Binti Kamarjalman

18652

Dissertation submitted in partial fulfillment of

the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

MAY 2015

Universiti Teknologi PETRONAS

32610 Bandar Seri Iskandar

Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Study of Catalyst Support Effect with Nickel Promoter in Thermocatalytic Decomposition of Methane for Hydrogen Production

by

Syazana Binti Kamarjalman

18652

A project dissertation submitted to the

Chemical Engineering Programme

Universiti Teknologi PETRONAS

in partial fulfilment of the requirement for the

BACHELOR OF ENGINEERING (Hons)

(CHEMICAL ENGINEERING)

Approved by,

_____

(Dr. Bawadi Abdullah)

UNIVERSITI TEKNOLOGI PETRONAS

BANDAR SERI ISKANDAR, PERAK

May 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

_____

SYAZANA BINTI KAMARJALMAN

ABSTRACT

Hydrogen production by thermocatalytic decomposition (TCD) is one of the most promising method to produce CO_X-free hydrogen as a source of renewable and sustainable energy. Thermocatalytic decomposition of methane requires an active functioning catalyst and support. Thus the need to study on the best catalyst support as well as its combination of the active component in order to design a catalyst with a high catalytic performance for the decomposition of methane in hydrogen production is necessary. The investigations started by synthesizing the catalyst using Aluminium Nitrate Hydrate, Al $(NO_3)_3.9H_2O$, Cerium Nitrate Hexahydrate, $Ce(N0_3)_3.6H_2O$, Magnesium Nitrate Hexahydrate, $Mg(NO_3)_2.6H_2O$ as support and Nickel as the promoter via co-precipitation method. Nickel as a choice of promoter was considered due to its high catalytic activities and stability to withstand longer period of time under certain temperature. The synthesized catalyst would then be characterized using a Temperature-Programmed Reduction (TPR), studied using a Thermo gravimetric analyser (TGA), X-Ray Diffraction Analysis (XRD) to understand the structures, phases and other parameters such as average grain size and defects. The Scanning Electron Microscope (SEM) will be used to study the stability and the morphology of the fresh and spent catalyst. The Response Surface Methodology (RSM) is intended to obtain an optimal response. Finally, thermocatalytic decomposition of methane would be carried in a Tubular Furnace Reactor at a temperature range from 500^oC to 800^oC and the conversion of methane to hydrogen was measured. The operating conditions would be adjusted in order to understand and obtain a complete conversion of methane and yield a high percentage of hydrogen production.

ACKNOWLEDGEMENT

First and foremost, I would like to express my deepest appreciation and undying gratitude towards my supervisor, Dr. Bawadi Bin Abdullah, for his constant kind guidance, help, assistance and encouragement throughout the entire duration of my entire Final Year Project. It is indeed my good fortune to be placed under his supervision for he is no doubt inspiring, knowledgeable, patience, and a very experience figure in the chemical engineering department of Univerisit Teknologi PETRONAS (UTP).

The course and project assigned by UTP during the final year project is a good opportunity and coverage to apply our knowledge which we have learned throughout our entire period of studying chemical engineering. Besides, I would also like to thank UTP for providing up-to-date equipment and conducive laboratory to conduct my final year project. Without a proper maintenance of the facilities, I may not be able to complete my project successfully.

Apart from that, I would also like to thank Dr. Abdus Salam, lecturer from the Chemical Engineering Department for his constant guidance and his sharing of knowledge and expertise throughout my entire period of studying in UTP.

Last but not least, I would also like to thank each individuals involved directly and indirectly in making this project a success.

TABLE OF CONTENT

LIST ABBREVIATION AND NOMENCLATURES

Ni	Nickel
Al	Alumininium
Ce	Ceria
Mg	Magnesium
EDS	Energy Dispersive Spectrometry
SEM	Scanning Electron Microscopy
XRD	X-Ray Diffraction
TGA	Thermogravimetric Analyser
TPR	Temperature Programmed Reduction

LIST OF FIGURES

LIST OF TABLES

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Background of Research

There is an arising interest to convert Hydrogen (H_2) as a promising energy supply to powered vehicles as fuel in fuel cells. The reason for an alternative energy supply is due to the declination of crude oil reserves, where energy supply is changing from being primarily oil based to gas based instead. Apart from continuous increase in global population and economic development, another major challenge in providing more energy, is the increasing emission of greenhouse-gas (GHG). Contributors towards GHG emissions are mainly caused by combustion of fuels in attempt to produce energy and electricity. In order to overcome the problem of GHG, a sustainable solution would be to produce clean energy. Hydrogen production via renewable sources such as biomass has become the current interest due to its potential application in fuel cells, which also does not contain any hazardous materials, since combustion of hydrogen only produces water and are capable to power vehicles efficiently (Reddy et al, 2005).

FIGURE 1.1 Fuel Cells Powered Vehicle Cars (Toyota's Global, Green, Innovation and Environmental Technology, 2002)

In order to produce a CO_X-free hydrogen for energy source, Methane decomposition is suggested as one of the promising methods. However, methane decomposition on its own (non-catalytic) can only occur at very high temperature of more than 1200^oC in order to obtain a reasonable yield of hydrogen due to strong C-H bonding with methane. By using catalyst, the operation temperature can be reduced and thus making Thermocatalytic decomposition (TCD) as one of the potential methods for obtaining hydrogen from methane apart from steam reforming and partial oxidation. TCD is identified as an upcoming alternative process for hydrogen production. The reason why TCD is considered among other method is because TCD could eliminate the need for water gas shift reaction. Methane decomposition also produces a useful byproducts, the deposited carbon which is normally used as nanomaterials (Li et al, 2006). Based on research of previous existing experiments, Nickel-based catalyst have been found to be an effective catalytic component in the decomposition of methane to produce hydrogen and carbon due to Nickel being more active and selective compare to other element (Venugopal et al, 2007). Three different promoters are also used to be doped with nickel in order to test and compare which are best at producing hydrogen via thermocatalytic decomposition of methane. An even more detailed comparison would be made and explained later in the literature review in order to understand further on the need for the development of catalyst in enhancing methane conversion to produce hydrogen.

1.2 Problem Statement

Non catalytic thermal cracking of methane would require a very high temperature of more than 1200^oC where else the use of a suitable catalyst would significantly help to reduce the temperature of the operation. The choice of catalyst and its support appears to be of great importance as it must meet some specific requirements in addition to the common demands of high selectivity, stability and activity, whilst at the same time help to reduce the decomposition temperature (Muradov et al, 2009). The use of transition metals catalyst such as Nickel is said to exhibit highest catalytic activities with the use of appropriate support. When active metal species are deposited on different supports, the catalytic performance ranging from the change of the structure or electronic state of the metal species would also

interact based on the type of support used. According to F.Solymosi (1994), methane decomposition depends on the type of support due to carbon migration occurring from metal support. A catalyst support is usually a solid with a high surface area to help maximize the surface area of a catalyst by distribution over the support. The help of support on catalyst convert the precatalyst to a more active state (Tanashev et al, 1998). Hence, there is a need to study the support and its combination of the active component in order to design a catalyst with a high catalytic performance for the decomposition of methane.

1.3 Objectives and Scope of Study

The objective of this research is to identify the effect of Nickel supported on Aluminium Oxide (Al_2O_3), Cerium (IV) Oxide, CeO_2, and Magnesium Oxide (MgO) as well as the identification of composition of the supported nickel catalyst that deliver stable performance for thermocatalytic decomposition of methane to produce hydrogen. The operating conditions and properties were also studied in order to compare the effectiveness of catalyst and the selected support.

In order to achieve the objectives, three scopes were set-up in this research. The three scopes are as follows:

i. To study the support effect on catalyst in hydrogen production

ii. To study the process of thermocatalytic decomposition of Methane for hydrogen production

iii. To study the catalytic activity of Nickel in hydrogen production

1.4 Relevancy of Project

As one of the current most promising energy source of the future, Hydrogen not only is the most stable and abundant energy source, it also does not contribute towards any greenhouse gases emission to the atmosphere. Decomposition of Methane into Hydrogen is a promising method to venture further into research and development

because it does not contribute to any greenhouse gas emissions. However, methane cracking process is considered not feasible in industries due to its high energy consumption in order to break the strong covalent bonds. Thermocatalytic decomposition of methane on the other hand introduces the use of catalyst as a medium to lower high energy consumption in order to break the covalent bonds to a gradually lower temperature. Transition metals has been proven to the most effective catalyst, and over the years, Nickel-based catalyst is capable of reducing the temperature for methane cracking process with an attractive percentage of hydrogen yield. With further research, thermocatalytic decomposition of methane can be applied widely in industry. Therefore, this research is significant for the development of an efficient catalyst capable of reducing the activation energy of the methane cracking process, and thus reducing the energy consumption.

1.5 Feasibility of Project

This final year project requires in-depth understanding and knowledge in the field of Chemical Engineering in order to perform detailed and comprehensive analysis in achieving the final results. This project revolves around three chemical engineering disciplines, which is reaction kinetics and mechanism, thermodynamics and quantum mechanics studies. The research phase of this project was conducted for the first 5 months. Extensive documents, thesis paper, journals and books has been referred as credible resources and validation of theories and experimental results.

The first 2 months were spent purchasing the required chemicals and the installation of a new tubular reactor and gas analysis system to measure the hydrogen yield. The experimental work began with synthesizing of catalyst and characterizing it with various analytical equipments for better understandings. The completion of this project is estimated to be completed in an 8 months period, and is an appropriate choice for a final year project.

CHAPTER 2

LITERATURE REVIEW

Continuous increase in global population and economic development towards providing more renewable energy is considered one of the major challenges. Current energy sources tends to produce greenhouse-gas (GHG) emissions. Main sources of GHG emissions are caused by combustions of natural gas (NG), coal and oil for heating, electricity production, transportation and industrial purposes. Oil production is accountable for 39% of hydrocarbon-related CO_2 emissions and NG for 20% with coal accounting for the remaining of 51%.

Due to all this hazardous release of GHG emissions, a research on new energy sources which do not emit or could at least gradually decrease the quantity of GHG emissions are highly focuses on.

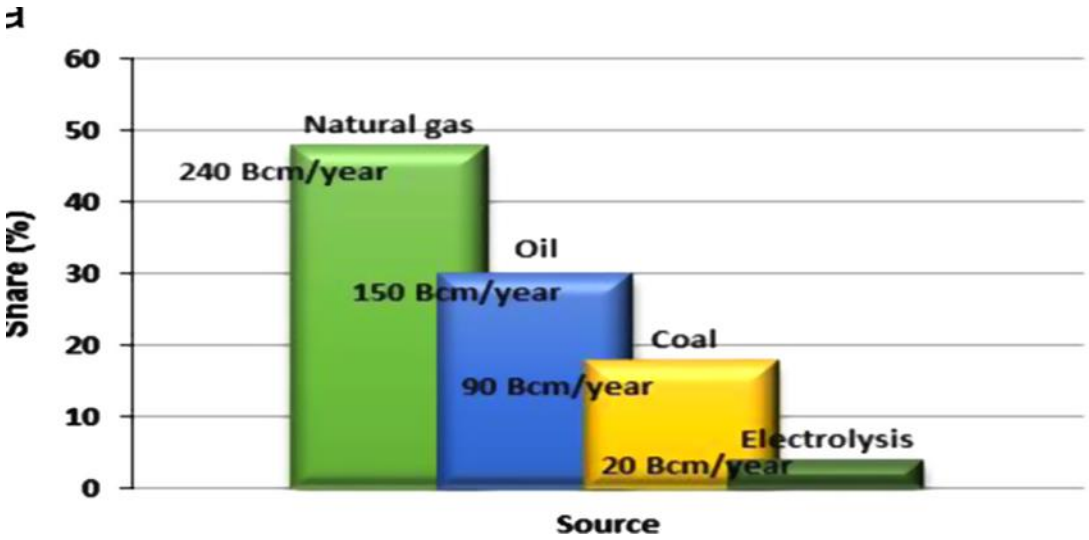


FIGURE 2.1 Worldwide Hydrogen Production by Sources (IIUM Engineering Journal, 2004)

Thus, the need to develop a clean, sustainable and cost-competitive renewable energy are highly considered. Hydrogen as a source of renewable energy is suggested mainly because hydrogen is the most abundant element in the universe and also appears to be one of the most promising energy vectors as it is considered to be clean and environmentally benign. The amount of energy produced during hydrogen combustion is higher compare to other fuel source on a mass basis, with a comparatively low heating value which is 2.8 or 4 times higher than gasoline or coal. Unfortunately, free hydrogen does not exist naturally on earth as usable gaseous form. Hydrogen production is made from primary source of water, natural gas, coal, petroleum or biomass. Thermocatalytic decomposition (TCD) of methane into carbon and hydrogen has recently attract researchers due the fact that TCD of methane does not produce CO_2. (Abbas. H. F, 2010). TCD has several advantages over other methods of producing hydrogen such as partial oxidation and steam reforming.

2.1 Available Methods

The three most conventional method of producing hydrogen consist of the steam reforming method, partial oxidation and autothermal reforming. Further elaborations on these methods are as follows:

2.1.1 Steam Reforming

Steam reforming and Partial Oxidation are thermochemical processes for hydrogen production via decomposition of methane, which is the main composition of natural gas with the highest C:H ratio, and with high process efficiency up to 50%. However, Steam Reforming causes high emissions of CO_X (1 mol of CO_2/mol of converted methane). This process requires more process energy. Steam reforming does not require the use of oxygen and it's operating temperature is operated at 700^{o}C to 1100^{o}C within a working pressure of 3 to maximum 25 MPa. However, carbon monoxide is the dominant gas released. Fuel reforming process on the other hand contains CO elimination by water gas shift reaction including selective CO oxidation with a post reaction mixture containing high CO even after purification is carried out.

Besides those conventional methods mentioned, water electrolysis process also has a potential to yield large amounts of CO_2 and CO as byproducts with hydrogen. In order to overcome this problem, hydrogen has to be purify, which would lead to an increase in production cost, and also exerts a great contribution to global warming.

2.1.2 Partial Oxidation

Partial Oxidation is an exothermic reaction which converts methane to hydrogen. The process is carried out by reacting the limited oxygen to avoid a complete oxidation which generates steam and carbon dioxide products. External heating of the reactor is not needed due to partial oxidation being an exothermic reaction. However, the process occurs at high temperature with formations of soots.

2.1.3 Autothermal Reforming

The process of autothermal reforming is a unique combination of both steam reforming as well as partial oxidation. Partial oxidation is needed to provide heat to the process where else steam reforming is needed to increase the hydrogen production which would result in a thermally neutral process. However, the process is normally conducted at a much lower pressure compare to partial oxidation. Just as partial oxidation, no external heat source is needed for the reactor since partial oxidation is exothermic and autothermal incorporates partial oxidation. However, a large amount of carbon monoxide is produced from the autothermal reforming process, and thus a water gas shift reactor is needed after the reforming section to covert carbon monoxide by reacting it with steam to hydrogen and carbon dioxide. Conventional methods of hydrogen production such as steam reforming, partial oxidation and autothermal reforming causes production of CO_2 at some point in the technological chain of the process due to the mixing of methane with water and oxygen.

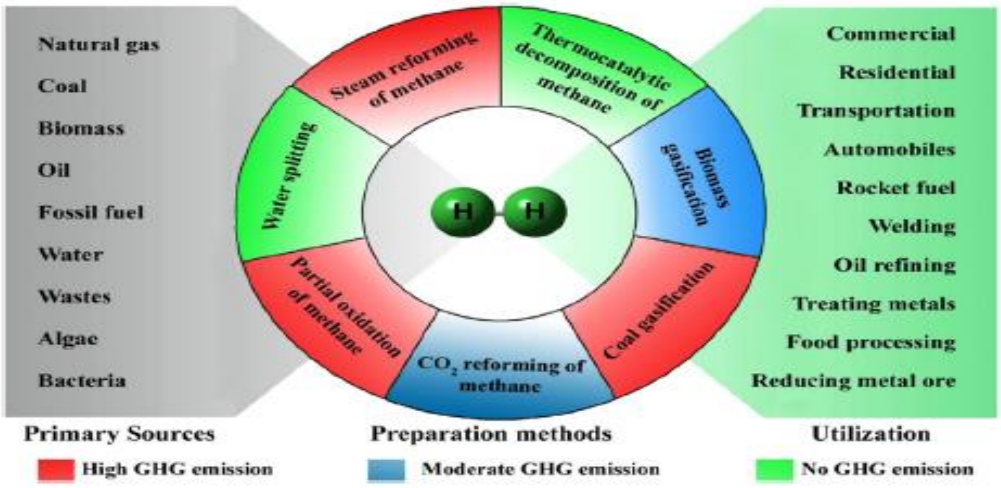


FIGURE 2.2 Schematic representation of the sources, preparation methods and utilization of hydrogen (IIUM Engineering Journal, 2004)

A new approach which have come to an interest towards producing hydrogen is by thermocatalytic decomposition of methane to carbon and hydrogen. In addition to producing hydrogen, the decomposition reaction could also produce a solid carbon nanostructured materials such as carbon nanotubes or carbon nanofibers byproduct, which could be sold (Li et al, 2006).

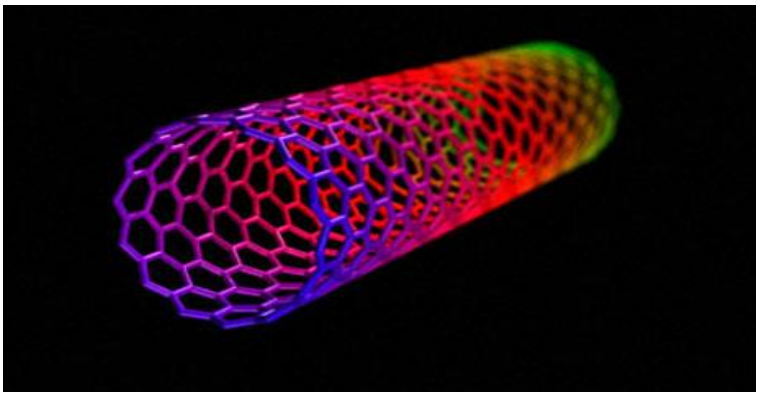


FIGURE 2.3 Structure of Carbon Nanotube (School of Chemical Engineering, Universiti Sains Malaysia, 2004)

$$CH_4 \longrightarrow C + 2H_2 \qquad (\Delta H_{298} = +74.8 \text{ kJ/mol}) \qquad \textbf{(1)}$$

However, thermocatalytic decomposition of methane is a moderately endothermic process (ΔH = +74.8 kJ/mol methane), it requires a high supply of heat to the reactor due to the strong C-H bonds. Methane molecule is held together by four strong carbon-hydrogen covalent bonds by sharing electrons. Carbon forms 4 bonds and more energy would be released thus making the molecule more stable. Therefore there is a need of high energy and temperature to break this bond.

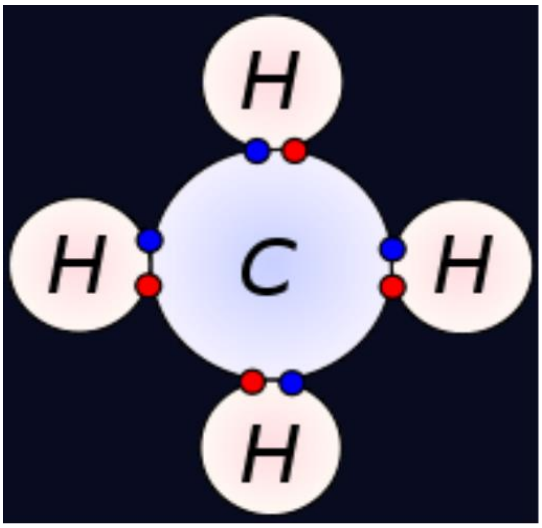


FIGURE 2.4 Covalent Bond in Methane (chemguide.co.uk, 2012)

Thus, a non-catalytic thermal cracking of methane would require a temperature of higher than 1200°C in order to obtain a reasonable yield. However, by using a catalyst, the temperature can be significantly reduced, depending on the type of catalyst used. The presence of catalyst will cause an alternative reaction mechanism with a slightly or much lower activation energy and transition state, and hence a higher number of molecular collisions can achieved the energy required to reach the transition state and enable a new lower temperature reaction to take place as indicated in figure 2.5.

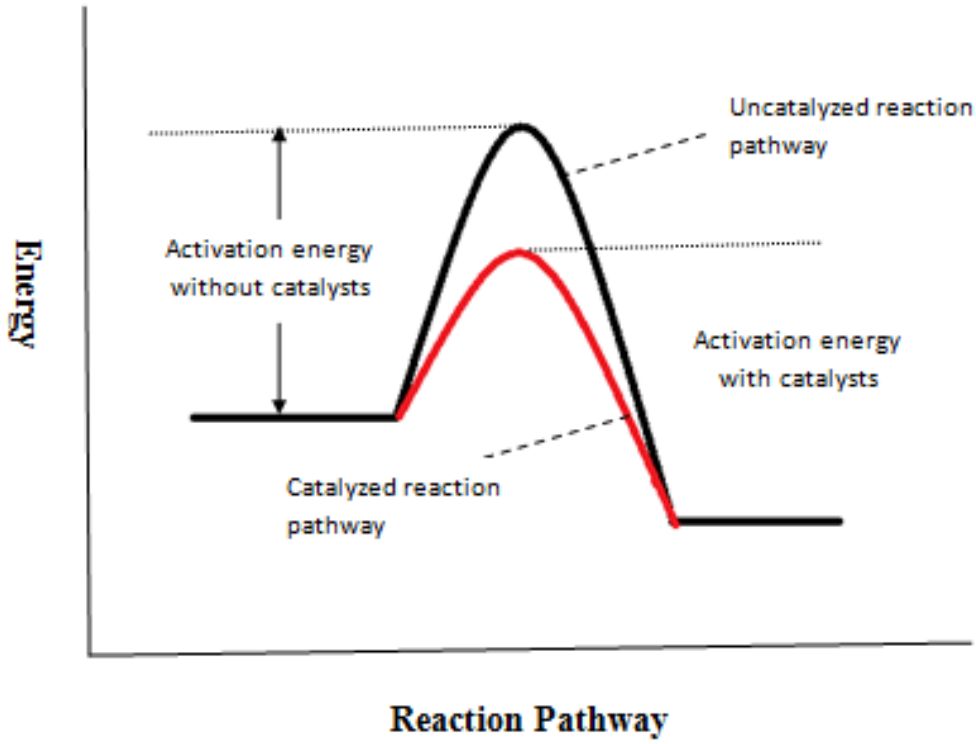


FIGURE 2.5 Potential Energy Diagram showing the effect of catalyst in chemical reaction by lowering the activation energy

The use of transition metals catalyst such as Nickel is said to exhibit highest catalytic activities and stability for few hours because Nickel is known as one of the active catalyst in thermocatalytic decomposition of methane. Although the decomposition of methane over metal-oxide transition metal catalyst such as Nickel produces high initial hydrogen concentration, their activity would drop rapidly over time because of surface deposition of carbon. When active metal species are deposited on different supports, catalytic performance can be attributed to the change of the structure or electronic state, based on the types and interaction of supports. Therefore, there is a need to study on the best support as well, and its combination of the active component in order to design a catalyst with a high catalytic performance for the decomposition of methane in hydrogen production (S.Takenaka et. al, 2001).

The three different types of support used on Nickel based catalyst are Aluminium Oxide (Al_2O_3), Cerium (IV) Oxide, CeO_2, and Magnesium Oxide (MgO). Al_2O_3, and MgO are well known supported metal oxide catalyst and are common and

widely used in various catalytic process because of their intrinsic acidity and ability to provide best carbon yield. Ceria on the other hand is a mixed metal oxides which based on research, is expected to improve catalytic performance. Ceria is also well-known for its ability to control automotive emissions and energy-related applications due to its ability to receive oxygen under oxidizing gas conditions and releasing oxygen under reducing gas conditions. The use of Ceria is not as widely used compare to Alumina and Magnesia, and thus would make a good comparison research between the other common supports chosen for highest hydrogen production.

One of the common problem faced by researchers in producing hydrogen via thermocatalytic decomposition is to get a suitable composition of catalyst which could yield 100% conversion with high hydrogen production.

Another limitation is the use of high temperature operating conditions in order to get the most of hydrogen production by means of complete conversion of methane. A very high energy usage is considered not feasible due to high power consumptions. Therefore, the need to study and develop on a more suitable compositions of Nickel based catalyst with different types of supports, along with a lower operating temperature are highly recommended in order to obtain the highest conversion of methane with the highest hydrogen production.

Moreover, productions of harmful by-products that causes greenhouse gas effects to the environment are also one of the limitations in current hydrogen production methods which needed to be overcome.

CHAPTER 3

METHODOLOGY

3.1 Research Methodologies and Project Flow

This chapter discusses the research methodology and project activities planned throughout the entire final year project and how it is conducted. This chapter also includes the choice of raw materials and chemicals used, the method which is employed to characterize the catalyst, the experimental setup to evaluate the performance of the catalyst as well as the key milestone and Gantt chart of the planned project. The flow of the research work is demonstrated in table 3.1.

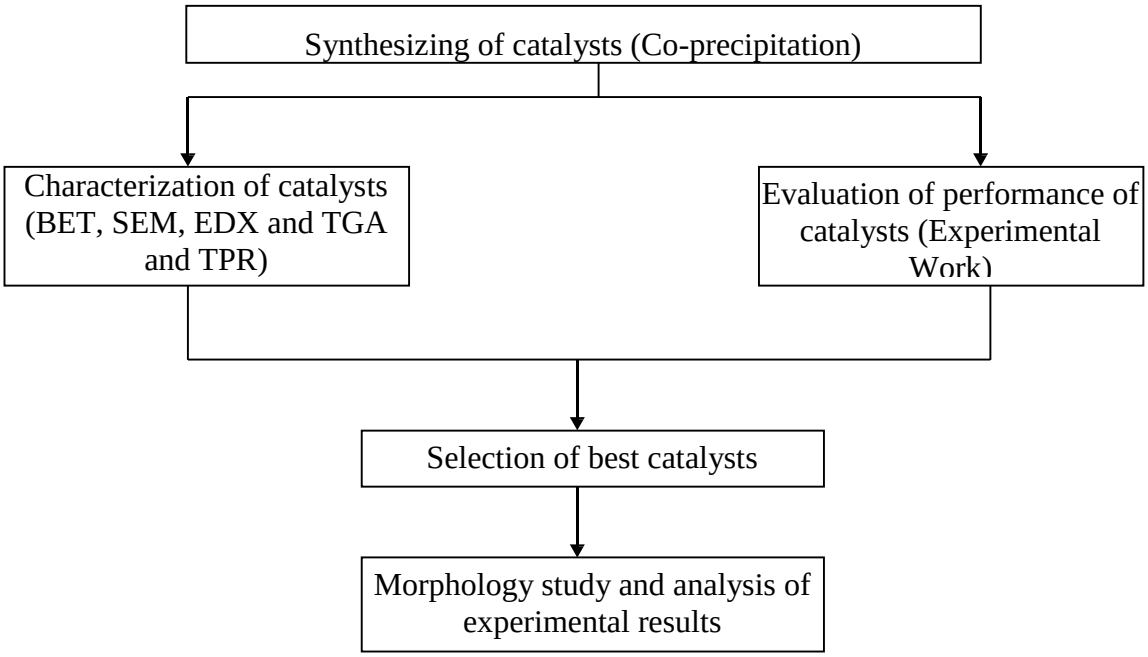


FIGURE 3.1 Flow of FYP Project

The experiment would be conducted on a three level basis:

i. Synthesize of catalyst

ii. Characterization of synthesized catalyst

iii. Reaction analysis of catalyst performance test in hydrogen production

3.1 Synthesize of catalyst

3.1.1 List of Raw Materials and Chemicals

In order to carry out the experiment, several raw materials and chemicals are prepared as follows:

a. Laboratory-Scale Pure Gases:

i. Methane (CH_4)

ii. Hydrogen (H_2)

iii. Nitrogen (N_2)

b. Chemicals:

i. Nickel (II) Nitrate Hexahydrate, $Ni(NO_3)_3.6H_2O$

ii. Cerium (III) Nitrate Hexahydrate, $Ce(NO_3)_3.6H_2O$ - (Support)

iii. Aluminium Nitrate, $Al(NO_3)_3.9H_2O$ - (Support)

iv. Magnesium Nitrate, $Mg(NO_3)_2$ - (Support)

v. Sodium Carbonate Decahydrate, $Na_2CO_3.10H_2O$ - (precipitating agent)

vi. Deionised Water

3.1.2 List of Equipments

In order to carry out this project, the types of equipment used are analytical and experimental. Fixed Bed Reactor will be the experimental equipment to be used in order to produce hydrogen via decomposition of methane. The analytical equipment planned to be used for characterizations are:

i. Temperature-programmed Reduction (TPR)

TPR is used for characterization of solid materials and are often used in the field of heterogeneous catalyst to determine the most efficient reduction condition. The oxidized catalyst precursor is subjected to the temperature rise while reducing gas mixture are flowed over it.

ii. Scanning Electron Microscopy (SEM) Analysis

SEM provides topographical and elemental information at magnifications of 10x to 300,000x, with virtually unlimited depth of field.

iii. Energy Dispersive X-Ray Spectroscopy (EDS)

It is an analytical equipment technique used for the elemental analysis or chemical characterization of a sample.

iv. Thermo Gravimetric Analyser (TGA)

TGA is a method of thermal analysis in which changes in physical and chemical properties of the catalyst are measured as a function of increasing temperature and time.

v. X-ray Diffraction Analysis (XRD)

X-ray diffraction (XRD) is a powerful non-destructive technique for characterizing crystalline materials. It provides information on structures, phases, preferred crystal orientations (texture), and other structural parameters, such as average grain size, crystallinity, strain, and crystal defects.

For the preparation of catalyst, the equipment required are listed as below:

i. Weighing Balance

In order to measure an accurate weight of chemicals and samples required for the process of catalyst synthesizing.

ii. Hotplate Magnetic Stirrer

The hotplate magnetic stirrer is used throughout the entire process of synthesizing catalyst. Each of the solutions prepared were stirred and heated for a homogenous mixture and to ensure well-dispersion phase within the catalyst.

iii. Furnace Chamber

The drying of the filtered catalyst and the pre-treatment calcination of catalyst was carried out in the furnace chamber. The calcination process is a process of heating up the catalyst at high temperature to ensure complete thermal decomposition.

3.1.3 Calculations for Preparation of Catalyst

In order to synthesize the catalyst and its' support, a suitable composition of Nickel and Aluminium Oxide (Al_2O_3), Cerium (IV) Oxide, CeO_2, and Magnesium Oxide (MgO) were proposed.

TABLE 3.1 Catalyst Composition

Sample	**Support**	**Catalyst Composition (wt%)**	
		Support	**Nickel (III) Oxide**
A	**Alumina**	90	10
B	**Ceria**	90	10
C	**Magnesium**	90	10

The first step in calculating an accurate amount of chemicals needed for catalyst synthesis, is by calculating the molecular weight and balancing the chemical reaction. The following chemical reactions are considered and balanced:

$2Ce(NO_3)_3.6H_2O + 2Na_2CO_3.10H_2O \rightarrow Ce(OH)_2.CO_3 + 4NaNO_3 + 30H_2O + H_2CO_3$ **(2)**

$2Mg(NO_3)_2.\ 6H_2O + 2Na_2CO_3.10H_2O \rightarrow Mg_2(OH)_2.CO_3 + 4NaNO_3 + 30H_2O + H_2CO_3$ **(3)**

$2Al(NO_3)_3.9H_2O + 3Na_2CO_3.10H_2O \rightarrow Mg_2(OH)_2.CO_3 + 6NaNO_3 + 46H_2O + H_2CO_3$ **(4)**

$2Ni(NO_3)_3.6H_2O + 2Na_2CO_3.10H_2O \rightarrow Ni_2(OH)_2.CO_3 + 4NaNO_3 + 30H_2O + H_2CO_3$ **(5)**

The calculation has been showed for 50 gm catalyst of Magnesium, Aluminum and Ceria, with different molar ratios as model calculation. The formula used to measure an accurate amount of weight of chemical is:

$$Weight\ of\ each\ Chemical\ (x) = \frac{Molar\ Ratio\ of\ 'x'\ X\ Molecular\ Weight\ (x)}{Molecular\ Weight\ of\ Associated\ Metal}\ X\ 50g \quad \textbf{(6)}$$

The weight of chemicals according to the molar ratios are as follows:

TABLE 3.2 Weight of Chemicals according to the molar ratios

Molar Ratio	**$Ce(NO_3)_3.6H_2O$**	**$Mg(NO_3)_2.6H_2O$**	**$Al(NO_3)_3.9H_2O$**	**$Ni(NO_3)_3.6H_2O$**	**$Na_2CO_3.10H_2O$**
M:N	-	33.60g	-	16.40g	50.33g
A:N	-	-	15.05g	34.95g	46.15g
C:N	37.32g	-	-	12.68g	51.9g

50g Basis

After getting an accurate amount of chemicals, the amount of water to be used to dilute with the weighed chemicals are according to the following formula:

$$Amount\ of\ Water = (\frac{Weight}{MW} \div Molarity)\ X\ (1000mL) \quad \textbf{(7)}$$

The molarity to be divided differs with support, metal and precipitating agent.

Support = 0.25 M

Metal = 0.75 M

Precipitating Agent = 0.5 M

The required total amount of Precipitating Agent, $Na_2CO_3.10H_2O$, also has to be calculated. The formula for the amount of weight of precipitating is:

$$W_T = W_1 + W_2 + W_3 \quad \textbf{(8)}$$

Here, W_1 = required amount of $Na_2CO_3.10H_2O$ for Mg precursor

W_2 = required amount of $Na_2CO_3.10H_2O$ for Al precursor

W_2 = required amount of $Na_2CO_3.10H_2O$ for Ce precursor

$$WT = 1.1\,X\left[\frac{Weight\ of\ Mg}{MW} + \frac{Weight\ of\ Al}{MW} + \frac{Weight\ of\ Ce}{MW} X \frac{2}{3}\right] X\ MW\ of\ W \quad \textbf{(9)}$$

The catalyst would be synthesized via co-precipitation method using sodium carbonate decahydrate, $Na_2CO_3.10H_2O$ as a precipitating agent. The precipitates will be aged for about 2.5 hours under vigorous stirring and then filtered and washed several times with water to remove the Na^+ and NO^{3-} ions. The precipitates would then be dried at 80°C for 12 hours and calcined at 600°C for 4 hours. The resulting catalyst were then grinded.

3.1.4 Co-precipitation Method

The first steps to synthesize catalyst via co-precipitation method is the preparation of the standard stock solution. The amount of chemicals weighed and dissolved are based on the formulas and calculations in the previous section. The crystal/solid chemicals were weighed and diluted in a volumetric flask. Next, the solution is stirred for 30 minutes with a hotplate magnetic stirrer at 200 rpm and 60°C. The method of co- were weighed and diluted in a volumetric flask. Next, the solution is stirred for 30 minutes with a hotplate magnetic stirrer at 200 rpm and 60°C. The method of co-precipitation requires time, for each of the mixture has to be titrated drop

by drop in order to enable a perfect mixing. Then, the mixtures were stirred at 60°C while 0.5 M of Sodium Carbonate Decahydrate, $Na_2CO_3.10H_2O$ were titrated drop by drop until the pH of the solution reaches a value of 9. The temperature will then be increased to 90°C and the solution will be stirred using the hotplate magnetic stirrer for 1 hour before being filtered and washed five times with deionised water. The sample will then be dried overnight or approximately 12 hours at 120°C. The dried up catalyst were then grinded and filtered up in a 100 μm sieve tray to get a finer size particle. After that, the grinded catalyst will then undergo a catalyst pre-treatment, which is the calcination process in a furnace chamber for 600°C for 6 hours in flowing air of 20mL/min to dry up any remaining moisture and to stabilize the catalyst. These steps were carried out for the preparation of:

i. 10% Ni 90% Alumina

ii. 10% Ni 90 % Magnesia

iii. 10% Ni 90% Ceria

The preparation of catalyst via co-precipitation solution is simplified as follows:

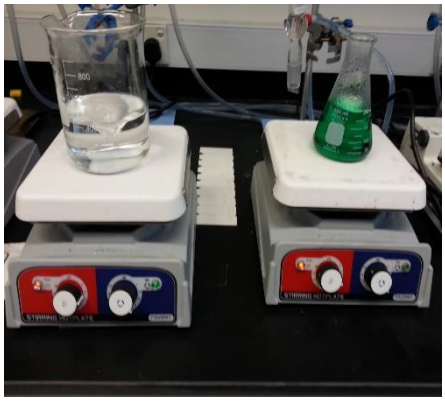


FIGURE 3.2 Stirring of Nickel and Alumina

1. The Preparation of Nickel and Magnesium before being titrated together.

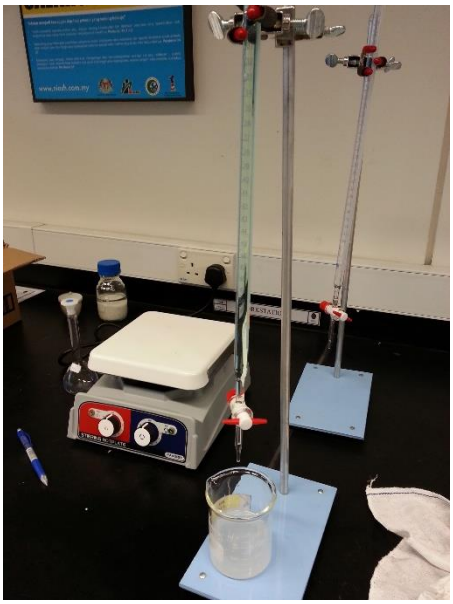


FIGURE 3.3 Titration of Nickel into Alumina

2. Titration of Nickel solution into Alumina

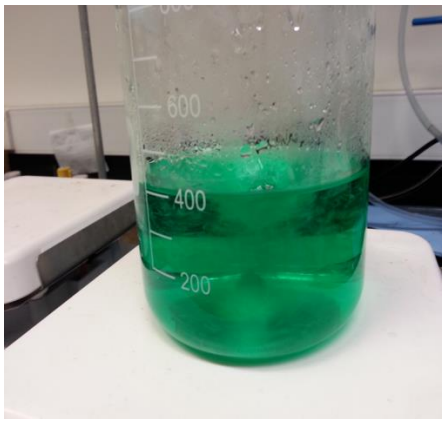


FIGURE 3.4 Stirring of the mixtures

3. Mixture solution of Nickel and Alumina were stirred to enable perfect mixing

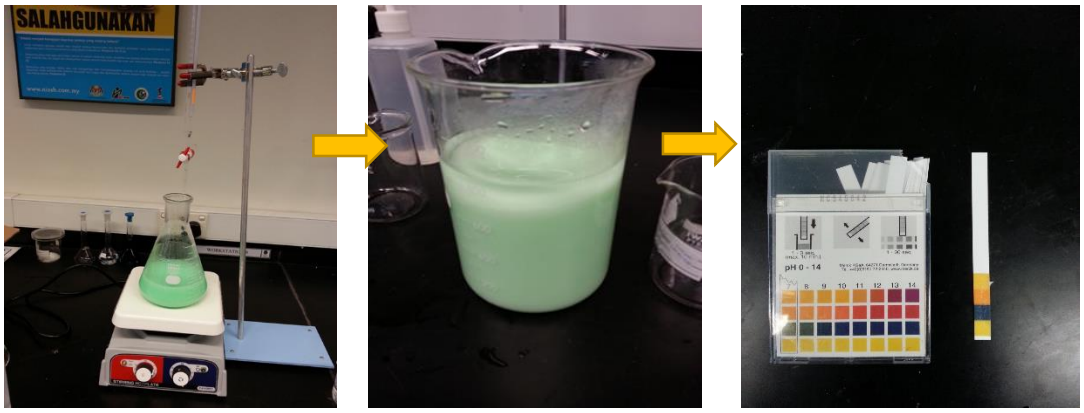


FIGURE 3.5 Precipitation of Mixture at Ph 9

4. The precipitate were stirred and heated for 1 hour until the solution becomes homogenous and reaches pH 9.

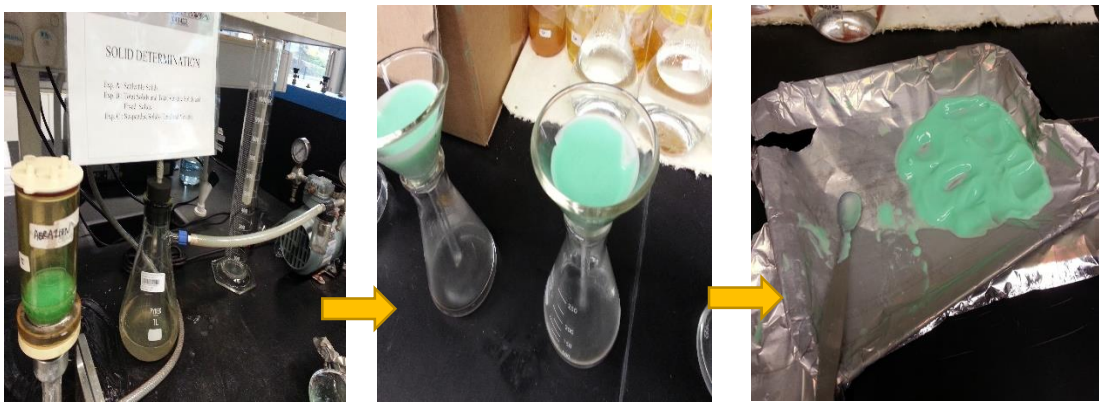


FIGURE 3.6 Filtration of Precipitate

5. Precipitation of Ni doped on alumina catalyst in Sodium Carbonate decahydrate is then washed and filtered several times to remove excess sodium carbonate and to be dried overnight.

FIGURE 3.7 Grinding of the dried up catalyst

6. The dried catalyst were grinded into smaller particles and filtered in a sieve tray equipment to obtain a 100µm size particle

FIGURE 3.8 Filtration of catalyst into smaller particles

7. Catalyst particles were then calcined in a furnace for 600^{o}C for 6 hours as a catalyst pre-treatment and finally ready to be tested and used.

FIGURE 3.9 Calcination Process as Catalyst Pre-treatment

3.2 Characterization of synthesized catalyst

The prepared catalyst would be characterized by a Temperature-Programmed Reduction (TPR). The Thermo gravimetric analyser (TGA) is used to study the stability of solids with respect temperature changes. Powder X-Ray Diffraction (XRD) patterns of all the samples will then be obtained in order to study the particle sizing. Finally, the Scanning electron microscope (SEM) will be used to study the morphology of the fresh and spent catalyst.

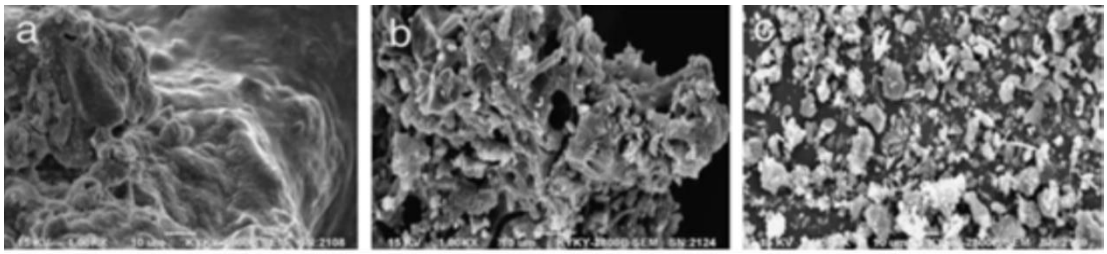


FIGURE 3.10 Scanning and Transmission Electron Microscope samples of catalyst (IIUM Engineering Journal, 2004)

3.3 Reaction analysis of catalyst performance test in hydrogen production

The thermocatalytic decomposition of methane would then be carried in a Fixed Bed-Gas Flow System. The experiment was carried out at 300^{o}C to 500^{o}C. Pure Nitrogen gas at 20 mL/min will be flowed through the reactor to create an inert atmosphere in the reactor. The synthesized catalyst will then be reduced in a flow of hydrogen gas at 30 mL/min at 500^{o}C for 1 hour. After reduction, the experimental set-up was flushed with pure Nitrogen until the gas chromatography system showed a complete disappearance of hydrogen gas.

The methane decomposition test rig system consist of 3 main components, which are:

i. Gas Mixing System

ii. Cracking Process in Reactor

iii. On-line Gas Chromatography

15 mL/min of highly pure methane gas (99.99% purity, *Sigma Aldrich*) will be diluted with 5 mL/min of Nitrogen gas (99.88% purity, *Sigma Aldrich)* before the gas mixture is introduced into the reactor. The flow of methane, hydrogen and nitrogen can be regulated by a mass flow controller located at the inlet stream. Thermocouple and temperature controller will be used to measure and monitor the temperature of catalyst in the reactor. The reactor effluent will be analysed using an online gas chromatography system (Hewlett Packard Series 6890) at the outlet of the reactor.

The performance of the synthesized catalyst can be measured and understood by analyzing the following properties:

i. Percentage of Hydrogen yield

ii. Conversion of Methane

iii. Operating Temperature of the cracking process

iv. Deactivation rate of catalysts

The catalyst will then be tested again using TPR and the outlet gas were collected and analyzed using Gas Chromatography (GC). The conversion of methane to hydrogen will be measured. The optimum condition for catalyst could be studied using Response Surface Methodology (RSM).

The Formula to measure the conversion and yield is as follows:

$$\text{Conversion (\%)} = \frac{Mole\ of\ Methane\ Reacted}{Mole\ of\ Methane\ Input} \text{ x } 100\% \quad \textbf{(10)}$$

$$\text{Yield (\%)} = \frac{Mole\ of\ Hydrogen\ Produced}{Mole\ of\ Methane\ Input} \text{ x } 100\% \quad \textbf{(11)}$$

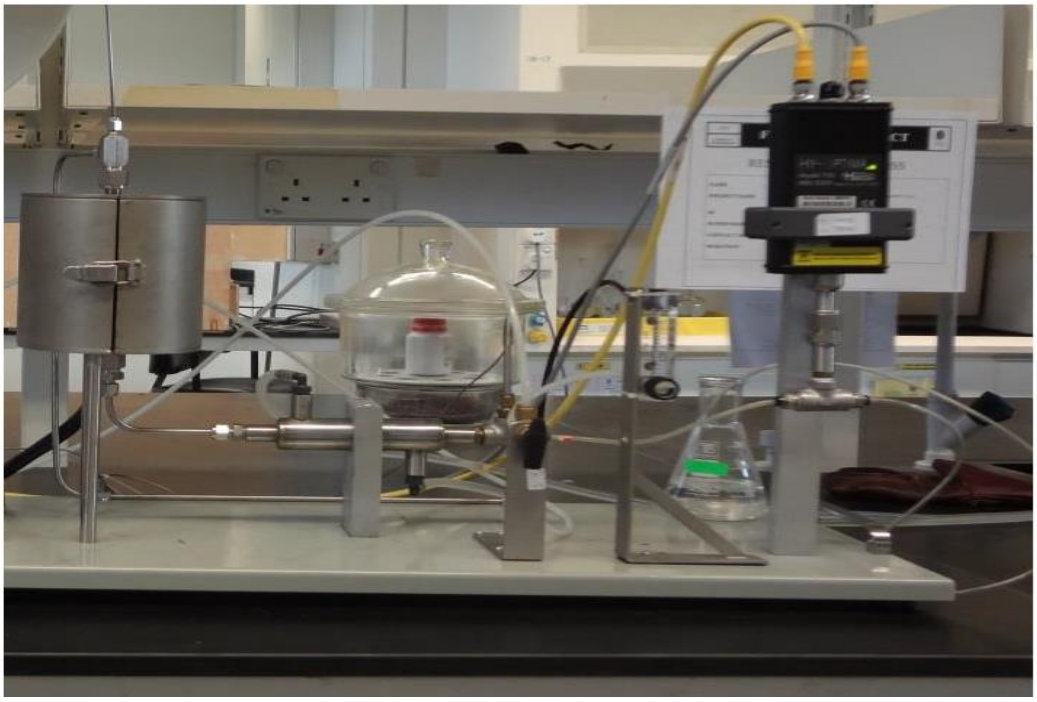


FIGURE 3.11 Fixed-Bed Gas Flow System

3.4 Key Milestone

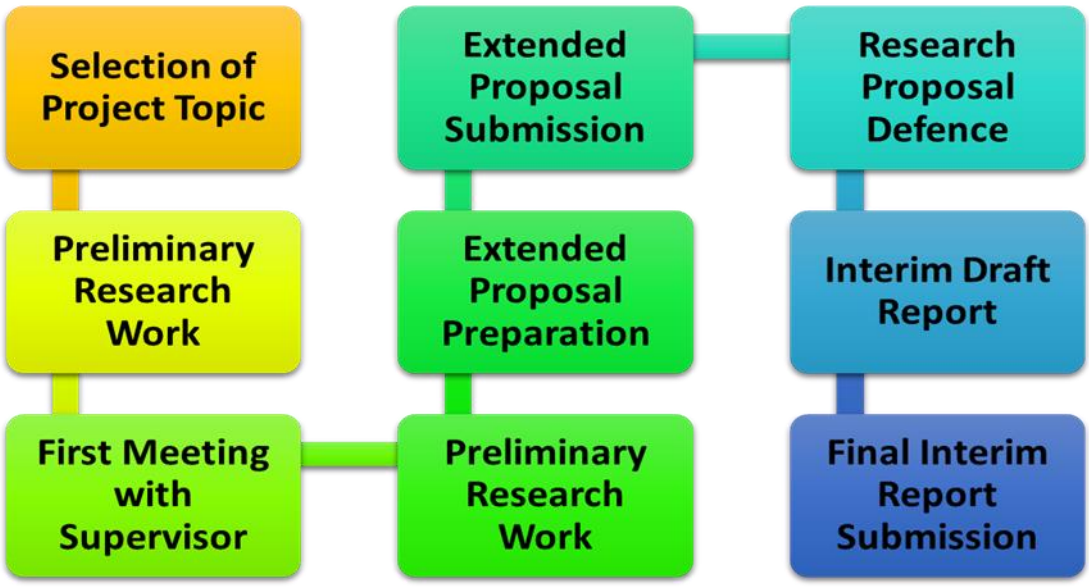


FIGURE 3.12 Key Milestone of Project

3.5 Gantt Chart of FYP 1

TABLE 3.3 Gantt Chart of FYP 1

No.	Detail / week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1.	Selection of Project Topic														
2.	Preliminary Research Work														
3.	Submission of extended proposal														
4.	Proposal Defense														
5.	Experimental work commences														
6.	Submission of interim draft														
7.	Submission of interim														

3.6 Gantt Chart of FYP 2

TABLE 3.4 Gantt Chart of FYP 2

No.	Detail / week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1.	Project Work Commence														
2.	Progress Report Submission														
3.	Project Work Commence														
4.	PRE-SEDEX														
5.	Draft of Final Report Submission														
6.	Dissertation Submission (Soft Bound)														
7.	Technical Paper Submission														
8.	VIVA														
9.	Dissertation Submission (Hard Bound)														

CHAPTER 4

RESULTS AND DISCUSSION

This chapter discusses the results obtained from the research work conducted and a detail discussion and analysis to provide a clear and significant understanding on thermocatalytic decomposition of methane for hydrogen production.

4.1 Characterization of Synthesized Catalysts

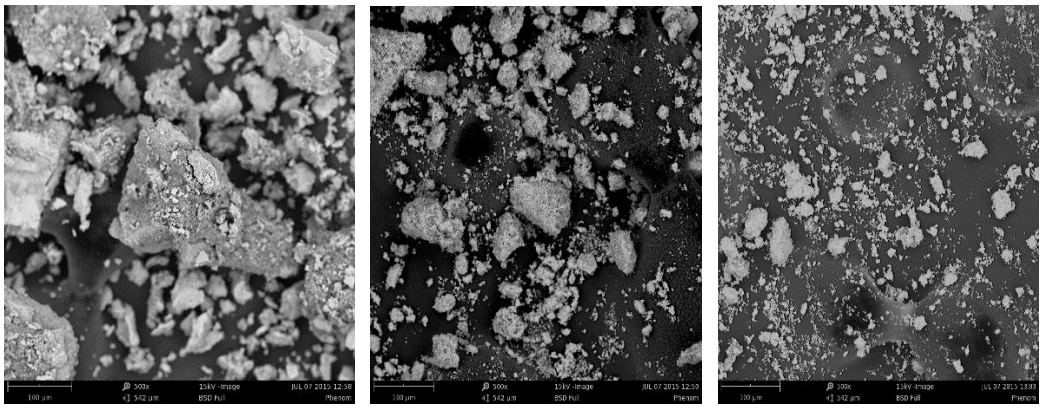
Characterization of catalyst is significant because it enables researchers to have a better insight on the physical properties and chemical properties of the catalyst. The physical properties of the catalyst may include pore size, surface area, morphology of the carrier and the geometry and strength of the support while the chemical properties may include the composition, structure, nature of the carrier and the active catalytic components. The catalyst developed and studied in this research is listed in table 4.1.

TABLE 4.1 Synthesized Catalysts

Types of Catalyst	Weight Percentage of Catalyst
(a) Nickel – Alumina	10% Ni 90% Alumina
(b) Nickel – Ceria	10% Ni 90 % Ceria
(c) Nickel - Magnesia	10% Ni 90% Magnesia

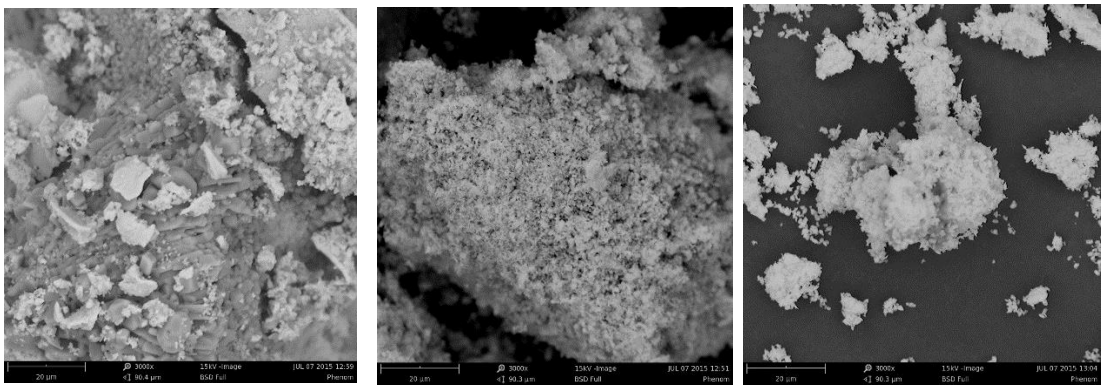
4.1.1 Scanning Electron Microscopy (SEM) Analysis

Due to limitations of availability of the Energy Dispersive Spectroscopy (EDS) mapping analysis, only the Scanning Electron Microscope were made available to study the morphology of the synthesized catalyst. (SEM) images were operated at an accelerating voltage from 5 to 30 kv. The samples were coated with graphite before the SEM images were taken at 500x, 1000x, 1500x, 3000x, 5000x, 10,000x and 15,000x magnification. SEM images represents the morphology of the catalyst with different magnification as follows:



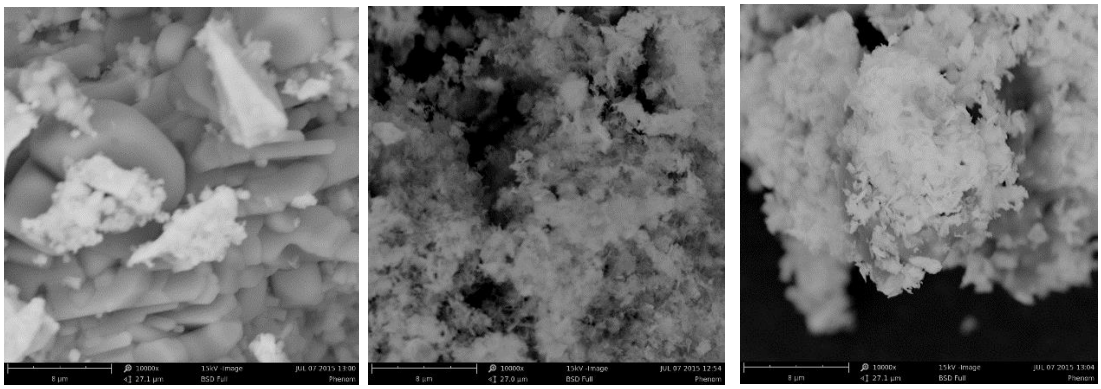
(a) Nickel-Alumina (b) Nickel- Ceria (c) Nickel-Magnesia

FIGURE 4.1 SEM Images of Catalyst at 500x Magnification (100 μm scale)



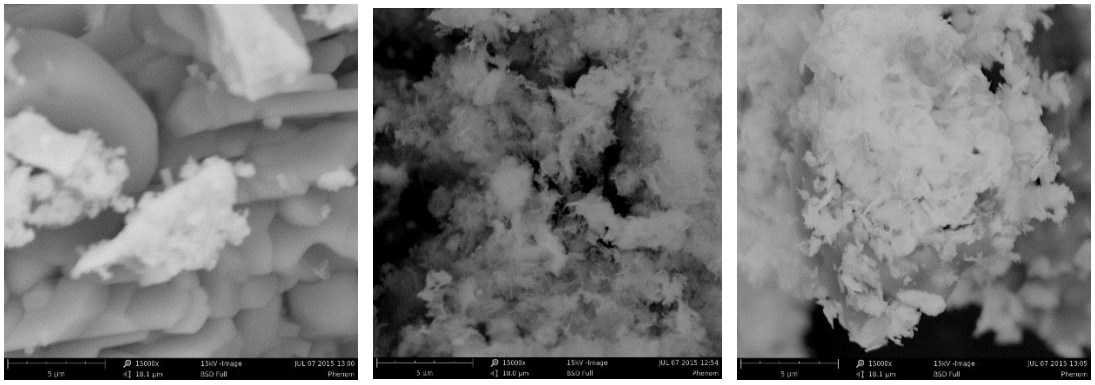
(a) Nickel-Alumina (b) Nickel- Ceria (c) Nickel-Magnesia

FIGURE 4.2 SEM Images of Catalyst at 3000x Magnification (20 μm scale)



(a) Nickel-Alumina (b) Nickel- Ceria (c) Nickel-Magnesia

FIGURE 4.3 SEM Images of Catalyst at 10,000x Magnification (8 μm scale)



(a) Nickel-Alumina (b) Nickel- Ceria (c) Nickel-Magnesia

FIGURE 4.4 SEM Images of Catalyst at 15,000x Magnification (5 μm scale)

SEM images indicates the catalyst which were prepared by co-precipitation method exhibits tetrahedron shape. It can be observed that smaller nickel particles were dispersed on the surface of Alumina support. Smaller particles size has been considered as one of the main factors for the development of effective catalyst for thermocatalytic methane decomposition process because large particles dispersion may promote the formation of carbon on the surface of the catalysts, and thus causing deactivation and sintering of the catalysts. Apart from that, the SEM images of the catalyst prepared by co-precipitation method reveals a surface with higher homogenous morphology.

The SEM images of Ceria shows small broken tubes connecting to each other indicating the absence of metal particles. The SEM image of Magnesia on the other hand indicates carbon nanotube being under develop with presence of black which are possibly caused by sintering of Nickel particles. The best supported catalyst observed was Ni/Alumina, based on the long carbon nanotubes observed, indicating a clear flow of reactants and products. The interpretation of the data above demonstrated that long-lived catalyst could be developed when the conditions of filamentous carbon growth are provided. Thus, it could be understood that the catalytic activity depended strongly on the type of support chosen for the highest conversion of methane to hydrogen.

4.1.2 Energy Dispersive Spectroscopy (EDS) Mapping Analysis

The use of EDS analysis is to determine the uniformity of dispersion of the elements on the catalyst. Apart from measuring the uniformity of dispersion, the EDS is also used to determine the atomic percentage of each individual element present in the catalyst, as well as the amount of metal precursor which have been incorporated onto the synthesized catalyst. The results of the EDS analysis is as follows:

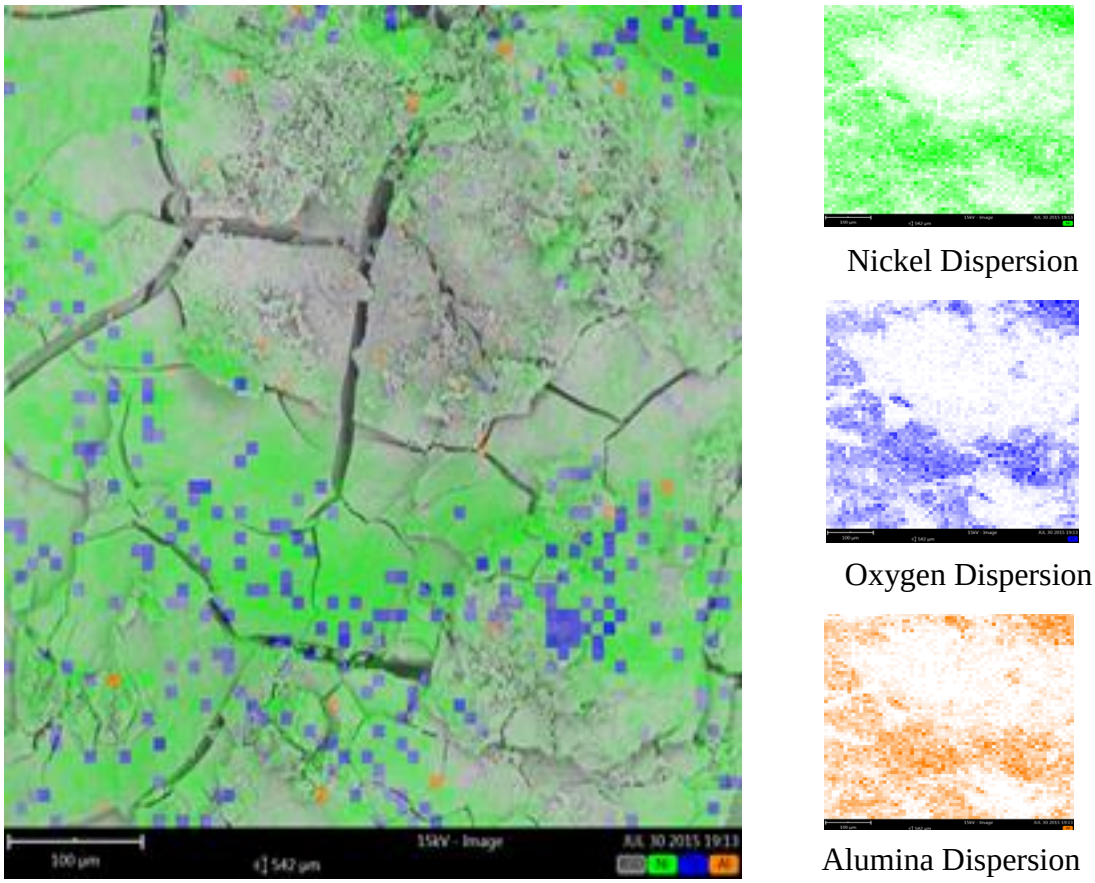


FIGURE 4.5 EDS Mapping for Ni-Al_2O_3 Catalyst

Table 4.2 Determination of Atomic Percentage of Ni-Al Catalyst

Element Number	Element Symbol	Element Name	Weight Concentration (%)
28	Ni	Nickel	70.4
8	O	Oxygen	22.2
13	Al	Aluminium	7.4

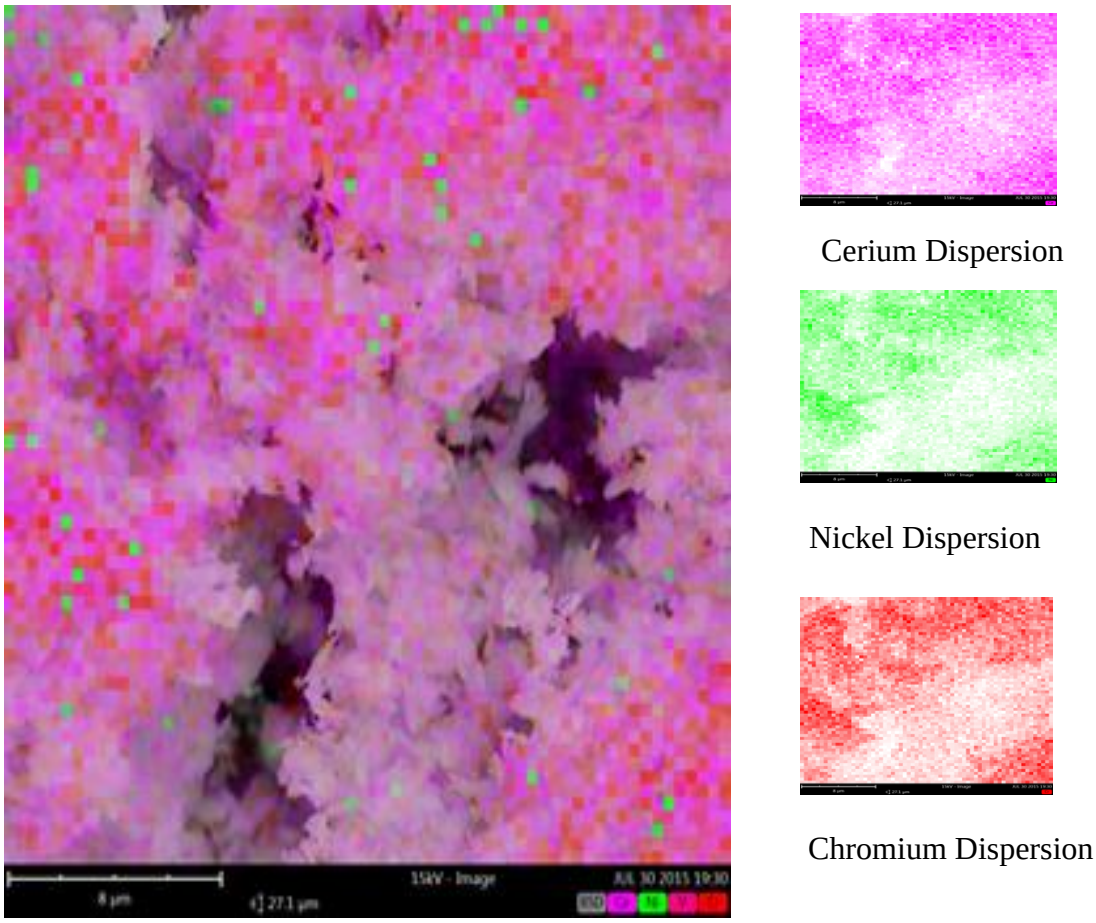


FIGURE 4.6 EDS Mapping for Ni-CeO_2 Catalyst

TABLE 4.3 Determination of Atomic Percentage of Ni-Ce Catalyst

Element Number	Element Symbol	Element Name	Weight Concentration (%)
58	Ce	Cerium	76.4
24	Cr	Chromium	2.2
28	Ni	Nickel	21.4

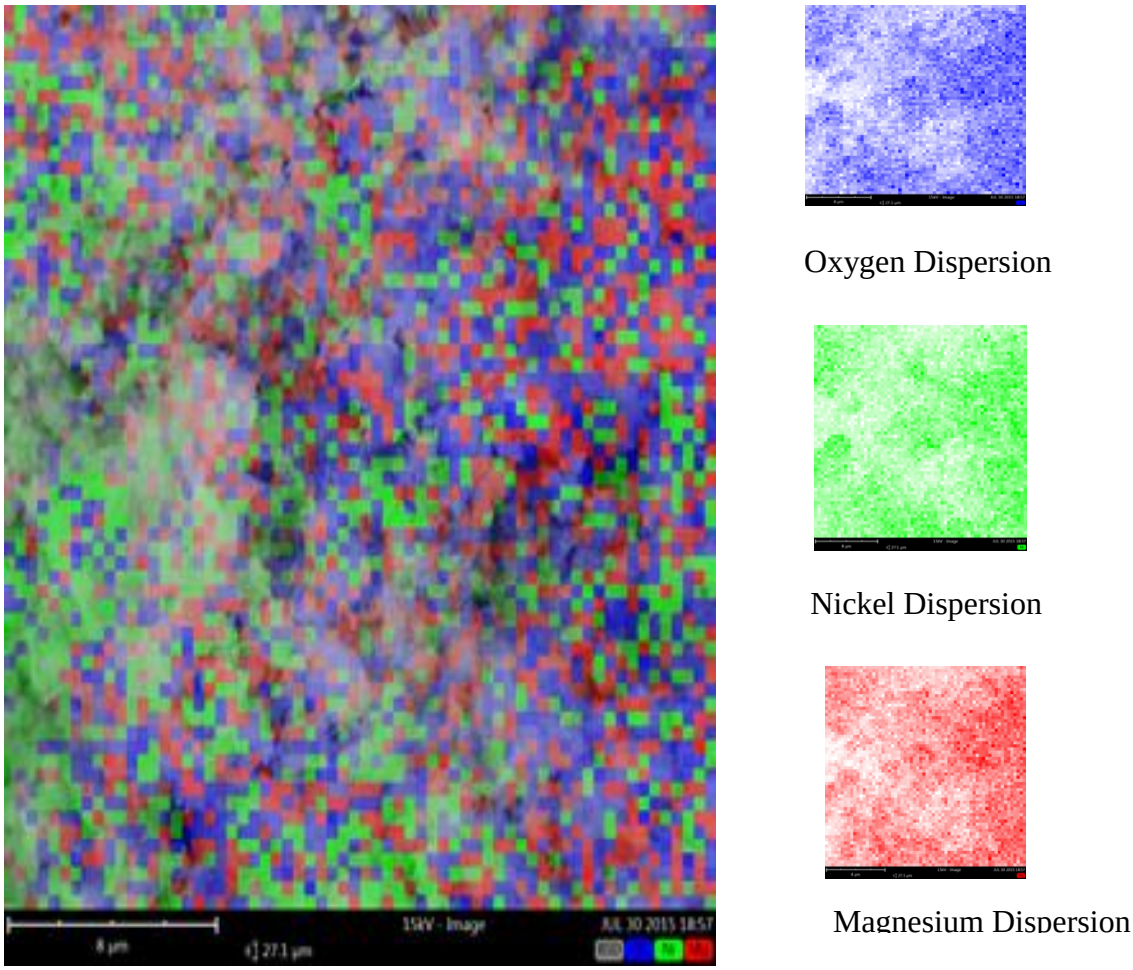


FIGURE 4.7 EDS Mapping for Ni-MgO Catalyst

TABLE 4.4 Determination of Atomic Percentage of Ni-Mg Catalyst

Element Number	Element Symbol	Element Name	Weight Concentration (%)
8	O	Oxygen	36.5
12	Mg	Magnesium	28.3
28	Ni	Nickel	35.2

The EDS mapping results of the three different catalyst and support indicates a uniform dispersion of support onto the catalyst synthesized. For the case of Nickel-Alumina catalyst, a uniform dispersion were observed and measured on the surface of catalyst with small range of error percentage as measured by the EDS. In the case of Nickel-Ceria catalyst, there is an unusual measurement of the element Chromium, which indicates contamination either in the synthesizing of catalyst or contamination in the EDS equipment itself. Characterization involving other analytical equipment can indicate the source of contamination either in the equipment or the catalyst itself with any other foreign element detected. Nickel-Magnesia shows the best dispersion of Nickel, Magnesia and Oxygen on the catalyst with an equal amount of all three elements measured. The uniform dispersion may strengthened the catalyst and enable an even more effective thermocatalytic decomposition of Methane to produce Hydrogen.

4.1.3 Thermal Analysis of synthesized catalyst (TGA)

The thermogravimetric analyser is used for the evaluation and investigation of weight loss, thermal behavior and structural decomposition of the catalyst. The catalyst samples were heated at a rate of 10^{o}C/min up to the temperature of 800^{o}C. The weight of the catalyst samples weighed were 0.1g and the TGA analysis performed under sweeping air atmosphere at 10mL/min.

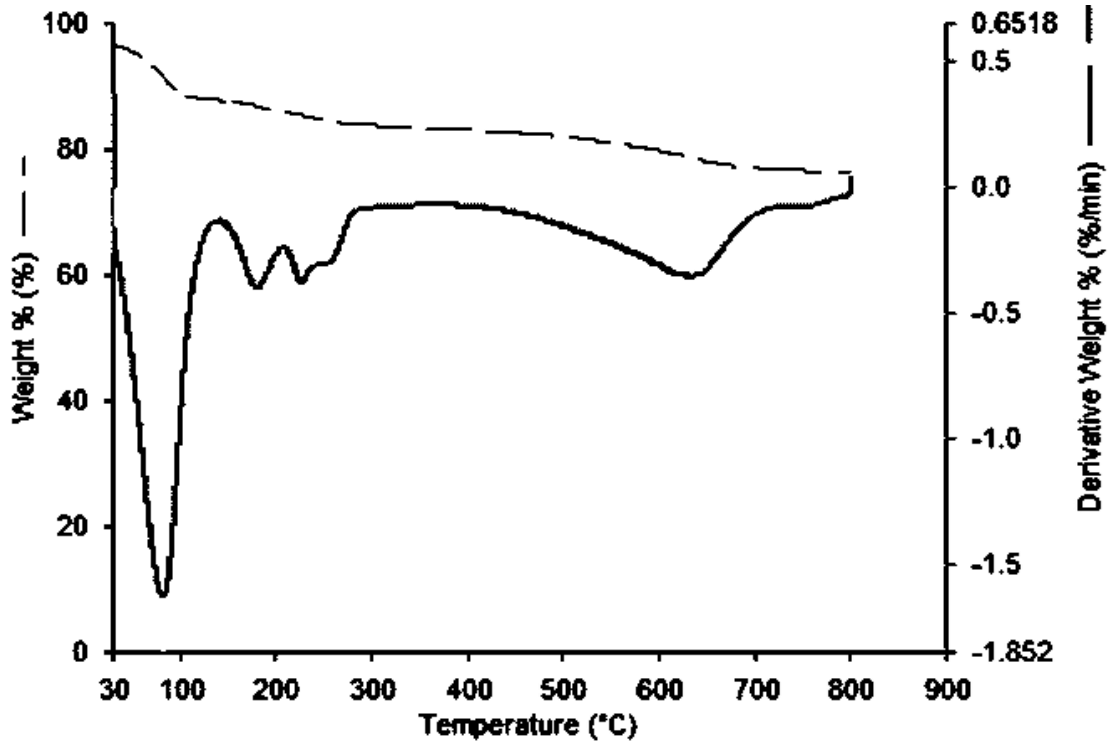


FIGURE 4.8 Weight Percentage (%) Versus Decomposition Temperature (°C) for Ni-Al_2O_3 Catalyst

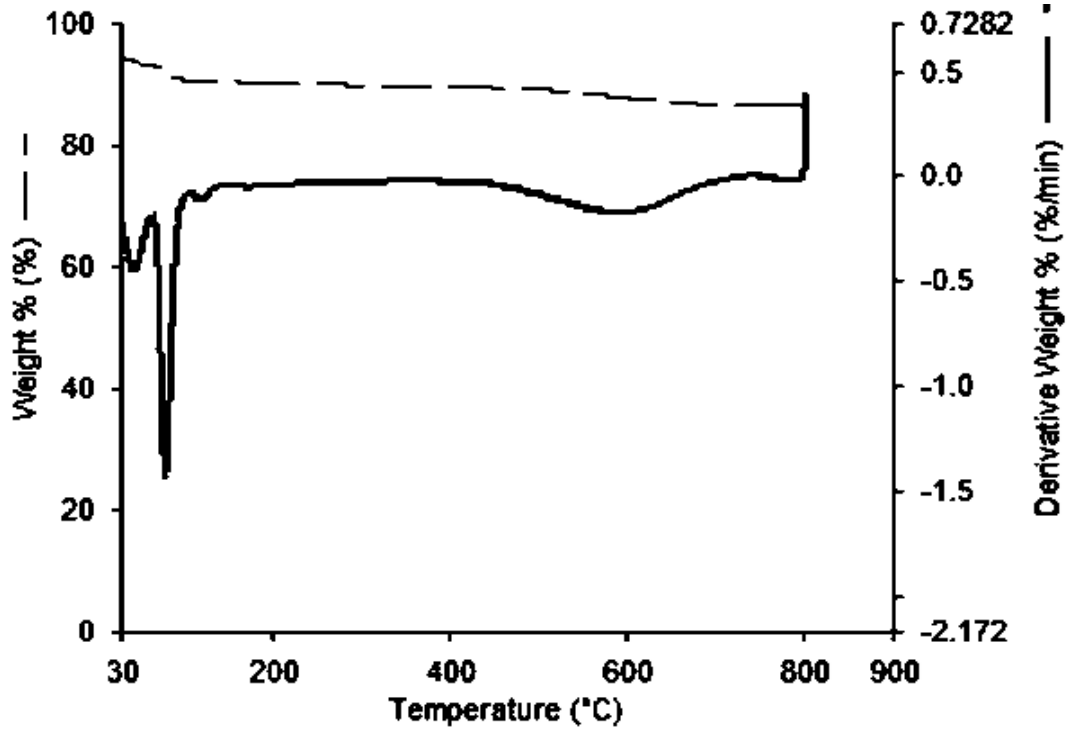


FIGURE 4.9 Weight Percentage (%) Versus Decomposition Temperature (°C) for Ni-CeO_2 Catalyst

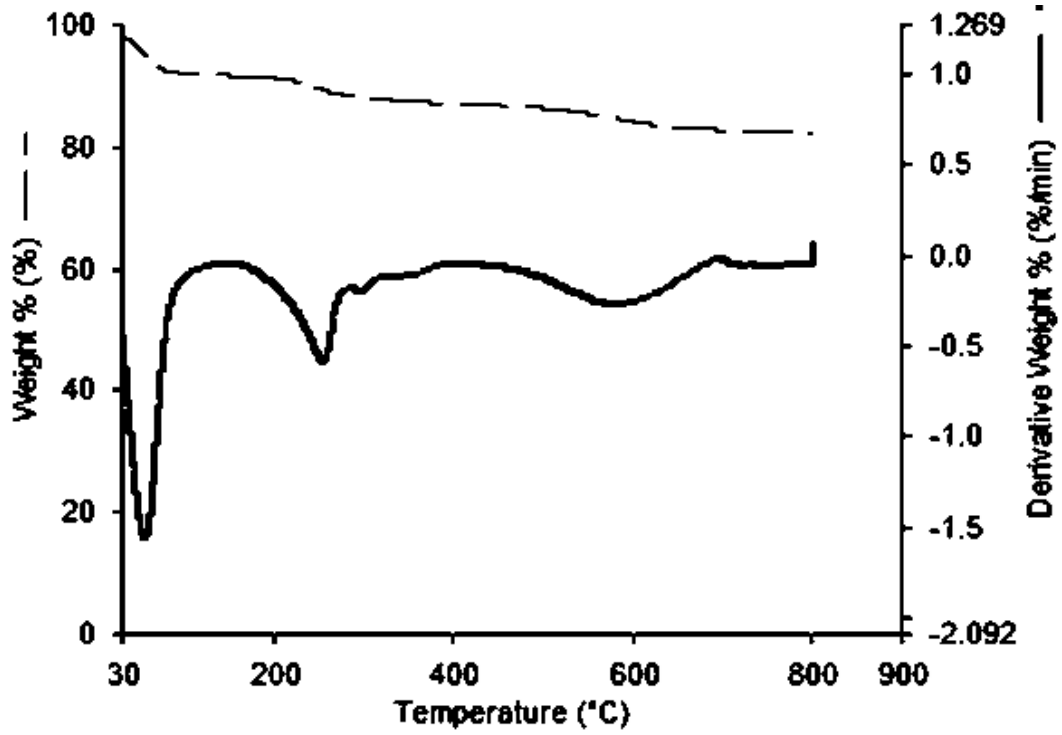


FIGURE 4.10 Weight Percentage (%) Versus Decomposition Temperature (^oC) for Nickel- MgO Catalyst

Figure indicates the relationship between weight percentages with the decomposition temperature for the calcined catalysts. All catalyst demonstrated good resistance towards decomposition even at temperature as high as 800^oC. One of the wanted characteristics of a good catalyst is the ability to withstand long term and high thermal stability to prevent decomposition of catalyst in methane cracking process. Nickel-Alumina Catalyst shows highest weight loss compare to Nickel-Ceria and Nickel-Magnesia. The reason for a higher weight loss could be due to different interactions between the Ni^{2+} and Al^{3+} species during the synthesizing process.

4.1.4 Temperature Reduction Programmed (TPR)

The H_2 – TPR technique equipment is used to study the reducibility behavior of the Metal Catalyst. The catalyst samples would undergo a pre-treatment process, where Nitrogen at 300^oC would flow at a flow rate of 20mL/min and at a ramping rate of 10^oC/min. A holding time of 30 minutes at a temperature rate of 300^oC is carried

out to remove any form of impurities. The temperature were then cooled to room temperature. The TPR analysis were carried out in a 5% H_2-N_2 with a flow rate of 20mL/min and heated to 800^{o}C with a ramping rate of 20^{o}C/min. The reduction profile were obtained and smoothen to understand the rate of Hydrogen consumption as a function of linearity temperature.

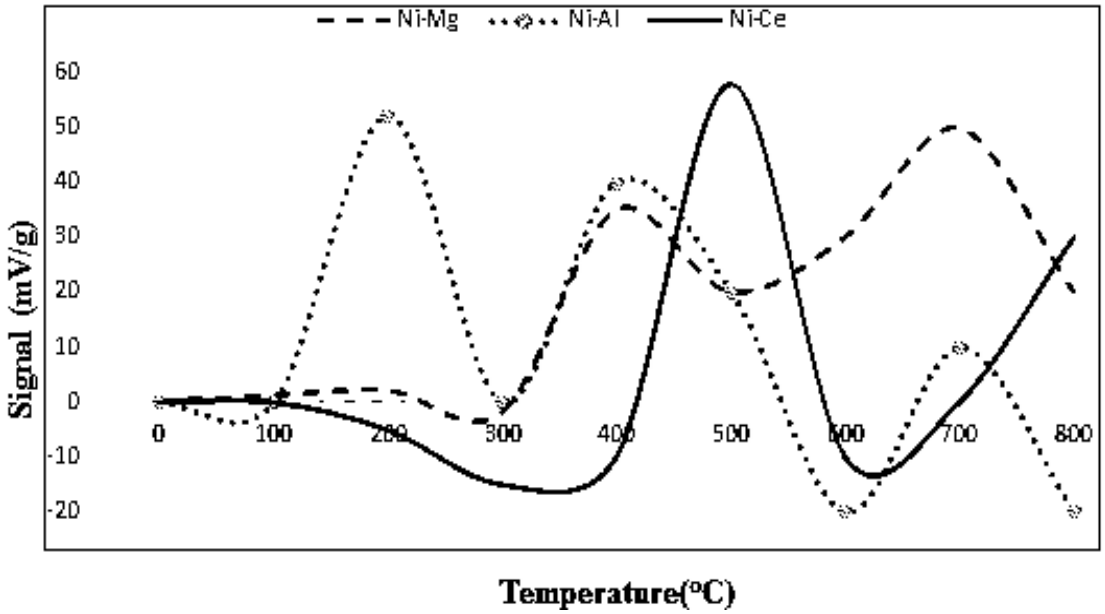


FIGURE 4.11 Temperature-programmed reduction profiles of catalyst

The TPR profiles of each catalyst based on figure shows the region where reduction and decomposition occurs. For the Nickel-Magnesium Catalyst, the first peak at 200^{o}C indicates the decomposition of nitrate. The second peak which corresponds to reduction of the Ni^{2+} was observed at 700^{o}C and indicating the dispersion of Nickel- Magnesium has stronger interaction with the support. For the case of Nickel-Alumina, the first peak was observed at 200^{o}C, where else the second and third at 400^{o}C and 700^{o}C respectively. This may be attributed to the reduction of Nickel species which interacts weakly with the Alumina support, and could be eliminated during the reduction process. Next, for the Nickel-Ceria catalyst, the reduction starts at 500^{o}C before being reduced to its metallic state.

4.1.5 X-Ray Diffraction (XRD)

The XRD is used for characterizing crystalline materials. For catalyst Ni-Al, the characteristic peaks of Nickel are obvious in the XRD spectrum of Nickel-Alumina support catalyst at (2θ=29.8°,36.2° and 42.2°) which indicates that Nickel is comparatively inconsistently loaded on this support. The rough surface indicates any form of sintering of catalyst and could potentially cause loss in catalytic activity. For the case of Nickel supported on Ceria, based on the XRD profiles, it was found that Ni-Ce is least crystalline and might potentially be caused by interaction between the contamination of Chromium Nickel, Cr_7Ni_3, found at (2θ=56.3). As a result, the catalyst was not stable during the reaction. Nickel supported on Magnesia which contains 10 mol% of NiO particle was not observed on the XRD profiles. This phenomenon indicates NiO is highly dispersed on MgO. According to Zein et.al, 2004, it is well known that MgO and NiO could form a solid solution due to a good mutual solubility between MgO and NiO, which later on could be brought by the results of XRD determination of the catalyst precursor NiO-MgO, which shows little to no difference in comparison to the pure MgO and NiO phase.

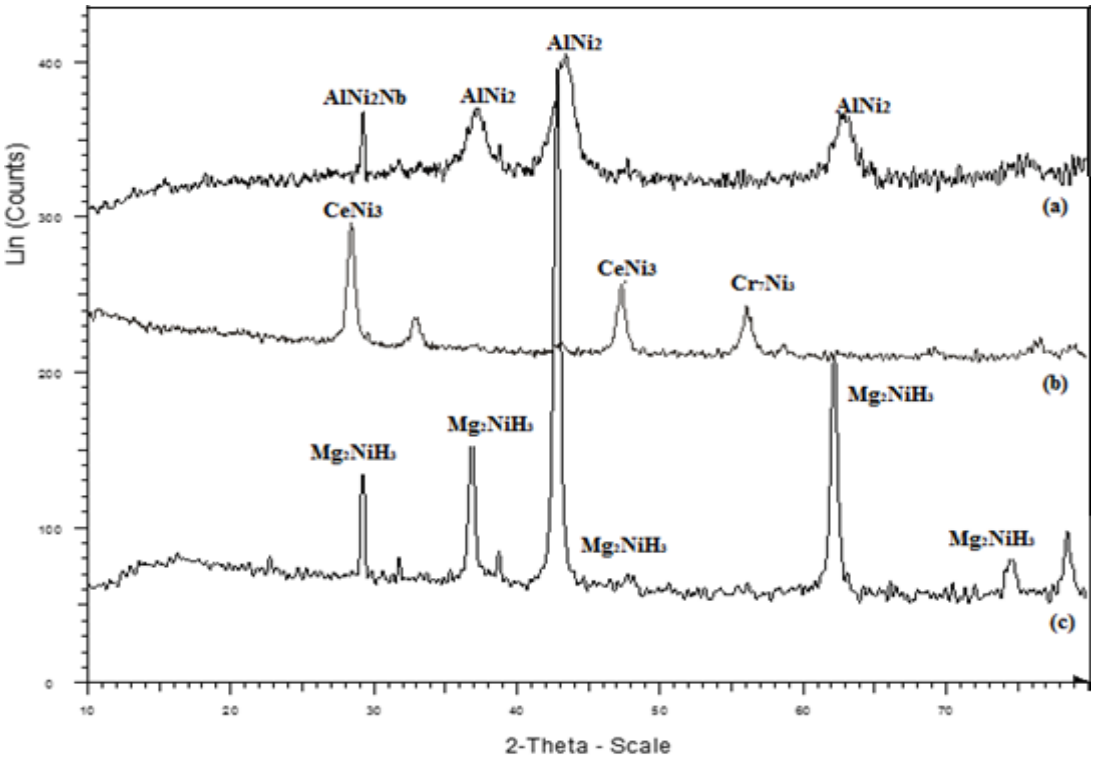


FIGURE 4.12 XRD Pattern of Fresh Catalyst containing (a) Ni-Al_2O_3, (b) Ni-CeO_2, (c) Ni-MgO

4.2 Reaction Performance

Based on figure , the conversion profile of methane based on each synthesized catalyst were shown as a function of time for the decomposition of methane to hydrogen and carbon within 4 hours on stream at 300°C, 400°C, and 500°C respectively. The stability and performance of each synthesized catalyst were studied based on the rate of methane conversion and hydrogen yield in time.

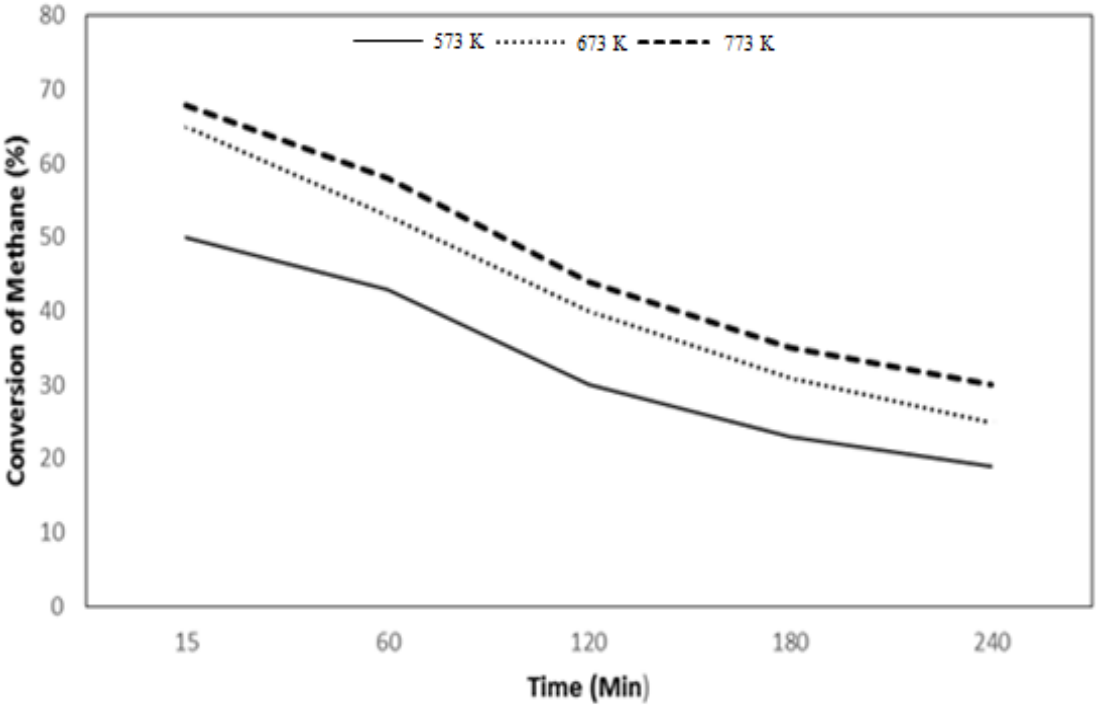


FIGURE 4.13 Conversion of Methane against time for (a) Ni-Al_2O_3 at Different Temperatures T=573K, 673K, 773K, and P=101.3kPa

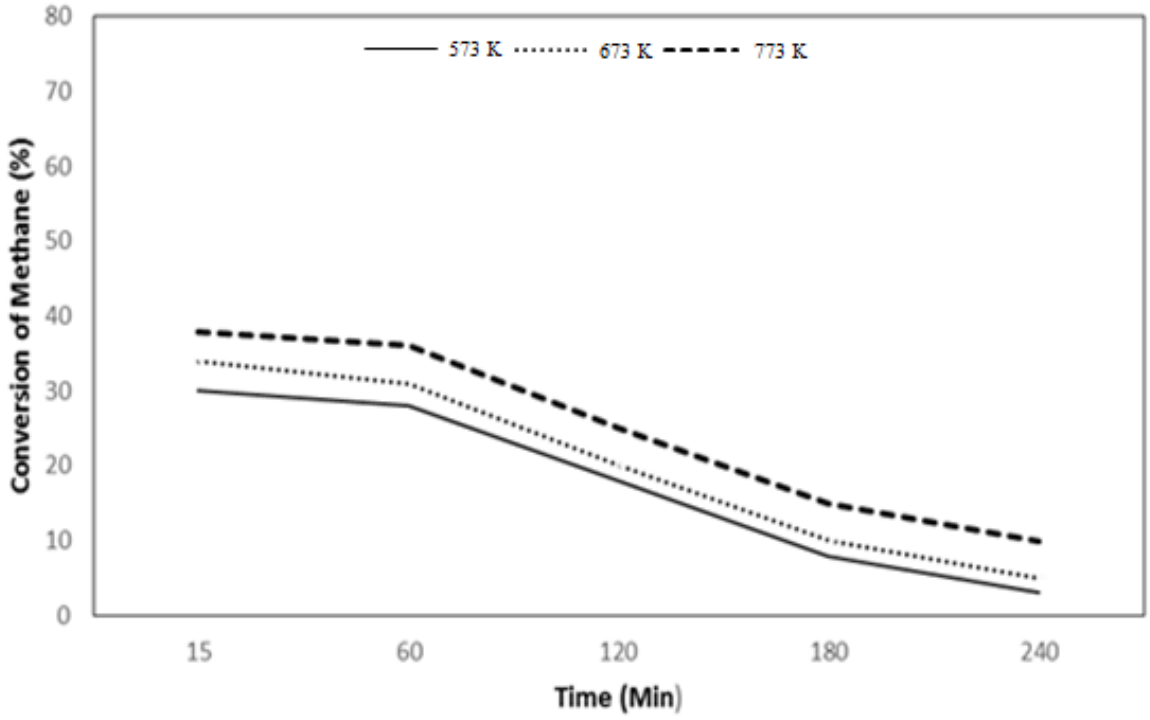


FIGURE 4.14 Conversion of Methane against time for (b) Ni-CeO_2 at Different Temperatures T=573K, 673K, 773K, and P=101.3kPa

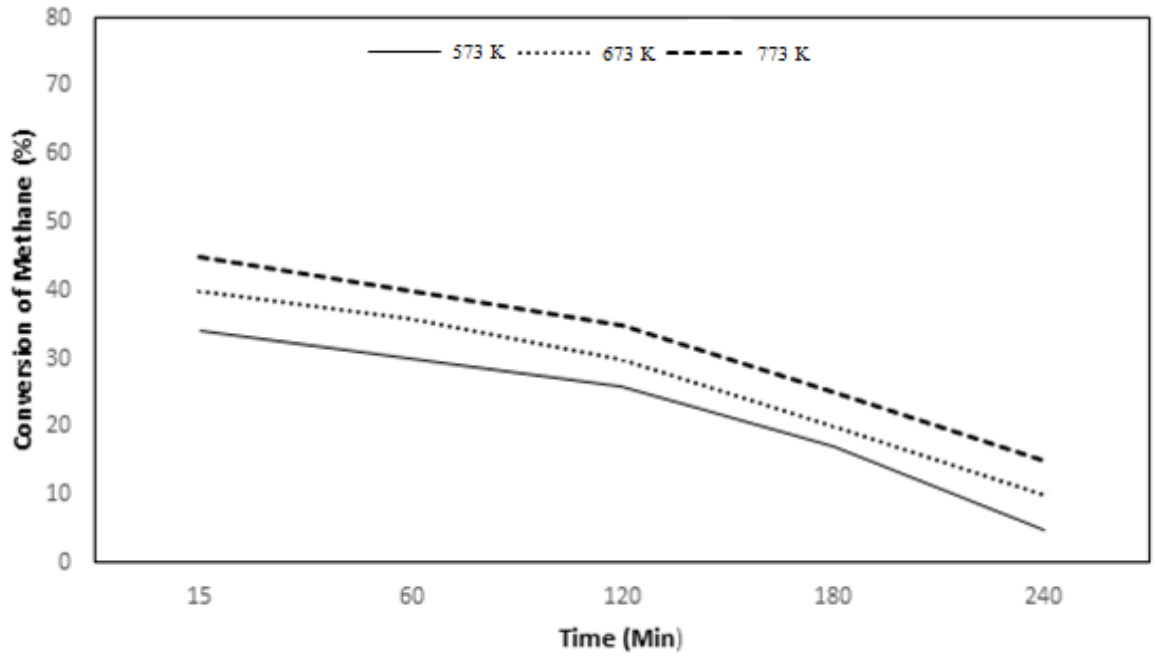


FIGURE 4.14 Conversion of Methane against time for (c) Ni-MgO at Different Temperatures T=573K, 673K, 773K, and P=101.3kPa

The reaction performance results shows as temperature increase, the catalytic activity would also increase significantly. The experimental studies indicates a relatively low value of methane conversion with decrease in temperature. The reason for this phenomenon is due to the reduced amount of energy available to break the strong covalent bond of C-H. The reaction performance also indicates a decrease in methane conversion over time due to carbon deposition on the active sites of the catalyst. The reason for such decrease could potentially be due to sintering and deactivation of the catalyst during the operation.

Next, the percentage of methane being converted observed has little deviation to similar percentage of hydrogen yield which suggested the production of CO_X free hydrogen gas. The reason is because all the reacted methane were heated at a relatively high temperature and causes methane to be fully converted into hydrogen without any production of by-products. Based on literature reviews and other researches, the result obtain is consistent and expected for all methane to be converted into pure hydrogen, which was reported by Zabadi et.al (2003) and Zhein et.al (2004).

The conversion of methane observed in the table below is after 240 minutes on stream. The lowest conversion of methane observed at 240 minutes on stream observed was for Nickel-Ceria catalyst. The reason could be as discussed earlier in the characterizations, where a contamination of Chromium were observed and causes reaction to be unstable. Another batch of Nickel-Ceria catalyst are currently being re-produced to be characterized and undergo testing to determine the catalytic activity of Nickel supported by Ceria.

The conversion of methane for Nickel-Magnesia observed at 240 minutes indicates a slightly higher conversion compare to Nickel-Ceria catalyst. This could be attributed to an evenly dispersion of Nickel and Magnesia within the structure of catalyst, as being tested under the EDS, thus enhancing the thermal stability of the catalyst at higher temperature by reducing the tendency of the catalyst to deactivate due to coking or sintering.

Nickel-Alumina catalyst shows highest conversion of methane and hydrogen yield after 240 minutes on stream as compared to the other 2 catalyst. This could be due to the capability of Ni-Al catalyst to accumulate carbon, thus contributing towards higher operational lifetime of the catalyst by making it less susceptible to deactivation and

coking. Apart from that, the uniform dispersion of Nickel and Alumina particles may have enable a higher interaction between the catalyst and methane to take place, even though some of the active sites of the catalyst may have been blocked by carbon particles. The rate of catalyst to be deactivated is also observed to occur as early as the first 2 hours. This could be due to the cracking of methane forming carbons deposited on the surface of the catalysts and causing deactivation in the catalytic activity of catalyst.

TABLE 4.5 Conversion of Methane and Hydrogen Yield after 240 minutes

Catalyst	**Temperature (°C)**					
	573		**673**		**773**	
	CH_4 Conv. (%)	**H_2 Yield (%)**	**CH_4 Conv. (%)**	**H_2 Yield (%)**	**CH_4 Conv. (%)**	**H_2 Yield (%)**
Ni-Ce	3	3	5	5	20	20
Ni-Mg	5	5	10	10	13	13
Ni-Al	15	15	25	25	30	30

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Inconclusion, the objective of this research which was to study the catalyst support effect with Nickel promoter in thermocatalytic decomposition of methane for hydrogen production is achieved. The three different types of support would theoretically yield different methane conversion and hydrogen production based on the highest catalytic activity, attractive carbon nanotubes as well as the longest catalyst lifetime.

The morphology study on the synthesized catalyst by SEM and EDS suggested that the characteristics study of catalyst could be understood based on the filamentous carbon formed and long-lived catalyst could be developed when the conditions of filamentous carbon growth are provided. Thus, it could be understood that the catalytic activity depended strongly on the type of support chosen for the highest conversion of methane to hydrogen. From the EDS characterization, it can be understood that a uniform dispersion of catalyst contributes towards a higher catalytic activity in the reaction performance and in a case where contamination occurs, the catalytic activity became unstable causing a lower methane conversion and hydrogen yield.

Under the TGA characterization, all catalyst demonstrated good resistance towards decomposition even at temperature as high as 800^{o}C which meets the characteristics of a good catalyst is the ability to withstand long term and high thermal stability to prevent decomposition of catalyst in methane cracking process.

The H_2 – TPR technique equipment were used to study the reducibility behavior of the Metal Catalyst and the TPR profiles of each catalyst shows the region

where reduction and decomposition occurs in order to understand the reduction and decomposition process.

The XRD provides information on structures, phases, preferred crystal orientations (texture), and other structural parameters, such as average grain size, crystallinity, strain, and crystal defects.

Based on the reaction performance carried out, the conversion profile of methane based on each synthesized catalyst were shown as a function of time for the decomposition of methane to hydrogen and carbon within 4 hours on stream at 300^{o}C, 400^{o}C, and 500^{o}C respectively. The stability and performance of each synthesized catalyst were studied based on the rate of methane conversion and hydrogen yield in time. The amount of hydrogen produced is estimated to be high with a suitable choice of compositions of catalyst and its support, which based on research would be the choice of Nickel and Alumina support. The high percentage of hydrogen yield would then be a solution for the search of renewable and sustainable energy of the future.

5.2 Recommendations

The study for an alternative energy production is an ongoing research. There will be new possibilities, equipments and methods in the future to ensure an even more promising outcome. In term of the development of catalyst where it's activation energy could be reduced further, further research could be carried out and performed in order to optimize the production process and catalyst in any possible ways. To optimize thermocatalytic decomposition of methane, there are few recommendations:

i. Explore possibilities of using other metallic catalyst such as Copper or Iron.

ii. Explore possibilities of combining different transition metal support which would have an even higher thermal stability and higher catalytic activity.

iii. Explore the optimum working conditions of the reaction process, either in the concentration of standard stocks or reaction process conditions.

iv. Further research on thermocatalytic decomposition of methane for hydrogen production.

REFERENCES

Abbas, H., & Wan Daud, W. (2010). Hydrogen production by methane decomposition: A review. *International Journal of Hydrogen Energy*, vol. 35: pp. 1160-1190.

Ahmed, S. (2013). Catalytic decomposition of methane for hydrogen production using different types of catalysts. *Titrit Journal of Engineering Science*, vol. 20 (5): pp-19-23.

Choudhary, T., Sivadinarayana,C., Chusuei, C.C., Klinghoffer, A., & Goodman, D. (2001). Hydrogen production via catalytic decomposition of methane. *Journal of Catalysis*, 199(1), 9-18.

Guevara, J. C., Wang, J. A., Chen, L. F., Valenzuela, M. A., Salas, P., Garcia-Ruiz, A., Novaro, O. (2010). Ni/Ce-MCM-41 mesostructured catalysts for simultaneous production of hydrogen and nanocarbon via methane decomposition. *International Journal of Hydrogen Energy*, vol. 35 (8): pp. 3509-3521.

Herrera J., Resasco D., "Loss of Single-Walled Carbon Nanotubes Selectivity by Disruption of the Co–Mo Interaction in the Catalyst", *Journal of Catalyst*, 221(2), 354-364, 2004.

Iijima S., "Helical Microtubules of Graphitic Carbon", Nature, 354(6348), 56-58, 1991

Jin, L. J., Si, H. H., Zhang, J. B., Lin, P., Hu, Z. Y., Qiu, B., & Hu, Q. (2013). Preparation of activated carbon supported Fe-Al2O3 catalyst and its application for hydrogen production by catalytic methane decomposition. *International Journal of Hydrogen Energy*, vol. 38 (25): pp. 10373-10380.

Liao M., Au C., Ng C., "Methane Dissociation on Ni, Pd, Pt and Cu Metal (111) Surfaces - A Theoretical Comparative Study", *Chem. Phys. Lett*., 272(5-6), 445-452, 1997.

Longmeir, B., Gallimore, A., & Hershkowitz, N. (2012). Hydrogen production from methane using an RF plasma source in total non-ambipolar flow. *Plasma Sources Science and Technology*, vol. 21(1): pp.1-8.

Mohd Zabidi, N., Sharif Zein, S., & Mohamed, A. (2003). Hydrogen production by catalytic decomposition of methane. *Technology Cluster: Oil and gas*, vol. 3(2): pp. 3-9.

Momirlan, M., & Veziroglu, T. N. (2005). The properties of hydrogen as fuel tomorrow in sustainable energy system for a cleaner planet. *International Journal of Hydrogen Energy*, 30(7), 795-802.

Muradov, N. (2001). Thermo-catalytic CO2-free production of hydrogen from hydrocarbon fuels in DOE hydrogen program review. Maryland. USA: The National Renewable Energy Laboratory for the U.S. Department of Energy.

Saraswat, S., & Pant, K. (2012). Thermo catalytic decomposition of methane-A novel approach to COx free hydrogen and carbon nanotubes production over Ni/SiO2 catalyst. *Energy and Environmental Engineering Journal*, vol. 1(2): pp. 81-85.

Takenaka, S., Shigeta, Y., Tanabe, E., & Otsuka, K. (2003). Methane decompostion into hydrogen and carbon nanofibers over supported Pd-Ni catalysts. *Journal of Catalysts*, vol. 220 (2): pp. 468-477.

Tatyana, V., Lyudmila, B., Zinfer, R., Andrey, L., & Vladimir, A. (2003). Carbon capicious Ni-Cu-Al2O3 catalysts for high-temperature methane decomposition. Applied Catalysts A: General, vol. 247: pp. 51-63.

Uddin, M., Wan Daud, W., & Abbas, H. (2014). Co-production of hydrogen and carbon nanofibers from methane decomposition over zeolite Y supported Ni catalysts. Energy Conversion and Management, vol. 90: pp. 218-229.

Wang, G., Jin, Y., Liu, G., & Li, Y. (2013). Production of hydrogen and nanocarbon from catalytic decomposition of methane over a Ni-Fe/Al2O3 catalyst. *Energy and Fuels*, vol. 27 (8): pp. 4448-4456.

Wang, H., & Lua, A. (2013). Hydrogen production by thermocatalytic methane decomposition. *Journal of Heat Transfer Engineering*, vol. 34(11-12): pp.896-903.

Wu, H., Parola, V., Pantaleo, G., & Puleo, F. (2013). Ni-based catalysts for low temperature methane stream reforming: recent results on Ni-Au and comparison with other Bi-metallic systems. *Journal of Catalysts*, vol 3: pp. 563-583.

Zhang, J., Jin, L., Li, Y., & Hu, H. (2013). Ni doped carbons for hydrogen production by catalytic methane decomposition. *International Journal of Hydrogen Energy*, vol. 38: pp. 3937-3047.

Zhou, L., Guo, Y., & Hideo, K. (2014). Unsupported nickel catalysts for methane catalytic decomposition into pure hydrogen. *AIChE Journal, doi*: 10.1002/aic. 14487.

Zhou L., Ohta K., Kuroda K., Lei N., Matsuishi K., Gao L., Matsumoto T., Nakamura J., "Catalytic Functions of Mo/Ni/MgO in the Synthesis of Thin Carbon Nanotubes", *J. Phys. Chem. B*, 109(10), 4439-4447, 2005.

APPENDICES

I Preparation of Standard Stock Solution

Composition of Nickel and Aluminium Oxide (Al_2O_3), Cerium (IV) Oxide, CeO_2, and Magnesium Oxide (MgO).

TABLE I.1 Composition of Nickel and Aluminium

Sample	**Support**	**Catalyst Composition (wt%)**	
		Support	**Nickel (III) Oxide**
A	**Alumina**	90	10
B	**Ceria**	90	10
C	**Magnesium**	90	10

The following chemical reactions are considered and balanced:

$2Ce(NO_3)_3.6H_2O + 2Na_2CO_3.10H_2O \rightarrow Ce(OH)_2.CO_3 + 4NaNO_3 + 30H_2O + H_2CO_3$

$2Mg(NO_3)_2.\ 6H_2O + 2Na_2CO_3.10H_2O \rightarrow Mg_2(OH)_2.CO_3 + 4NaNO_3 + 30H_2O + H_2CO_3$

$2Al(NO_3)_3.9H_2O + 3Na_2CO_3.10H_2O \rightarrow Mg_2(OH)_2.CO_3 + 6NaNO_3 + 46H_2O + H_2CO_3$

$2Ni(NO_3)_3.6H_2O + 2Na_2CO_3.10H_2O \rightarrow Ni_2(OH)_2.CO_3 + 4NaNO_3 + 30H_2O + H_2CO_3$

The calculation has been showed for 50 gm catalyst of Magnesium, Aluminum and Ceria, with different molar ratios as model calculation.

The formula used to measure an accurate amount of weight of chemical is:

$$Weight\ of\ each\ Chemical\ (x) = \frac{Molar\ Ratio\ of\ 'x'\ X\ Molecular\ Weight\ (x)}{Molecular\ Weight\ of\ Associated\ Metal}\ X\ 50g$$

The weight of chemicals according to the molar ratios are as follows:

TABLE I.2 Weight of Chemicals to Molar Ratios

Molar Ratio	**$Ce(NO_3)_3.6H_2O$**	**$Mg(NO_3)_2.6H_2O$**	**$Al(NO_3)_3.9H_2O$**	**$Ni(NO_3)_3.6H_2O$**	**$Na_2CO_3.10H_2O$**
M:N	33.60 g	-	-	16.40g	50.33g
A:N	-	-	15.05g	34.95g	46.15g
C:N	37.32g	-	-	12.68g	51.9g

50g Basis

II Analysis of GC data

Calibration gas composition used:

i.	Oxygen	5%
ii.	Nitrogen	5%
iii.	Carbon Monoxide	4%
iv.	Methane	4%
v.	Hydrogen	4%

Collected gas samples were analysed separately for Hydrogen with Argon as the carrier gas after the analysis for Methane component was completed using Helium as the carrier gas. From gas chromatograph result, the mole fraction of hydrogen Y_{H2} with peak area A_{H2} are given by:

$$y_{H_2} = \left(\frac{y_{cal,H_2}}{A_{cal,H_2}}\right) \times A_{H_2}$$

$$CH_4 \rightarrow C + 2H_2$$

t=0 1 0 0 moles

t=t $1-X_{CH4}$ X_{CH4} $2X_{CH4}$ moles and total moles $= 1+2X_{CH_4}$

Thus,

$$y_{H_2} = \frac{2X_{CH4}}{1+2X_{CH_4}} \text{ and } y_{CH_4} = \frac{1-X_{CH4}}{1+2X_{CH_4}}.$$

Finally, we get from the relationships,

$$X_{CH4} = \frac{\frac{1}{2}\times y_{H2}}{\frac{1}{2}\times y_{H2} + y_{CH4}}$$

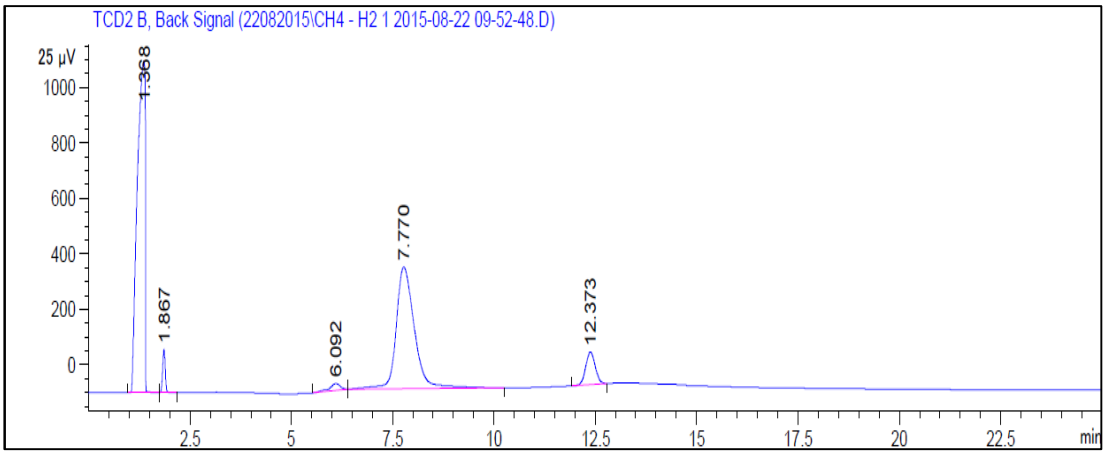


FIGURE I.3 Area Distribution from GC

TABLE I.2 Area Percent Report

Peak#	RetTime(Min)	Width(min)	Area[25µV*s]	Area %	Name
1	1.15	0.0000	0.0000	0.0000	He
2	1.368	0.2446	1.61243e4	48.75803	?
3	1.867	0.0690	681.38666	2.06086	H_2
4	6.092	0.2781	461.38211	1.39545	N_2
5	7.770	0.4747	1.38775e4	41.97255	CO
6	12.373	0.2569	1918.69641	5.80311	CH_4
7	16.642	0.0000	0.0000	0.0000	CO_2

III TGA Weight Percentage

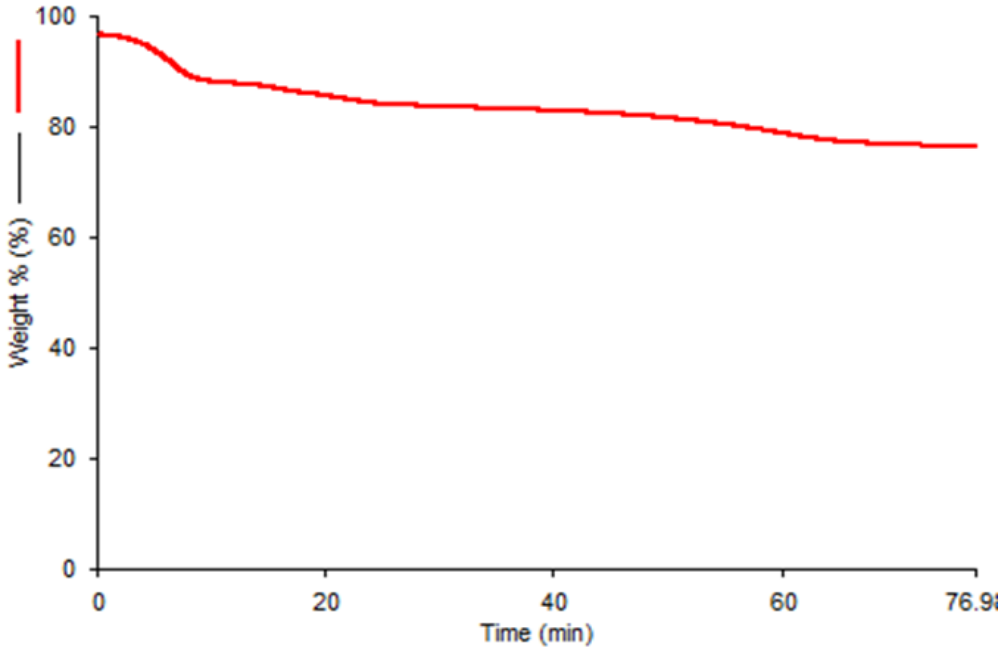


FIGURE A2.2 TGA rate of weight decomposition over time for Ni-Al

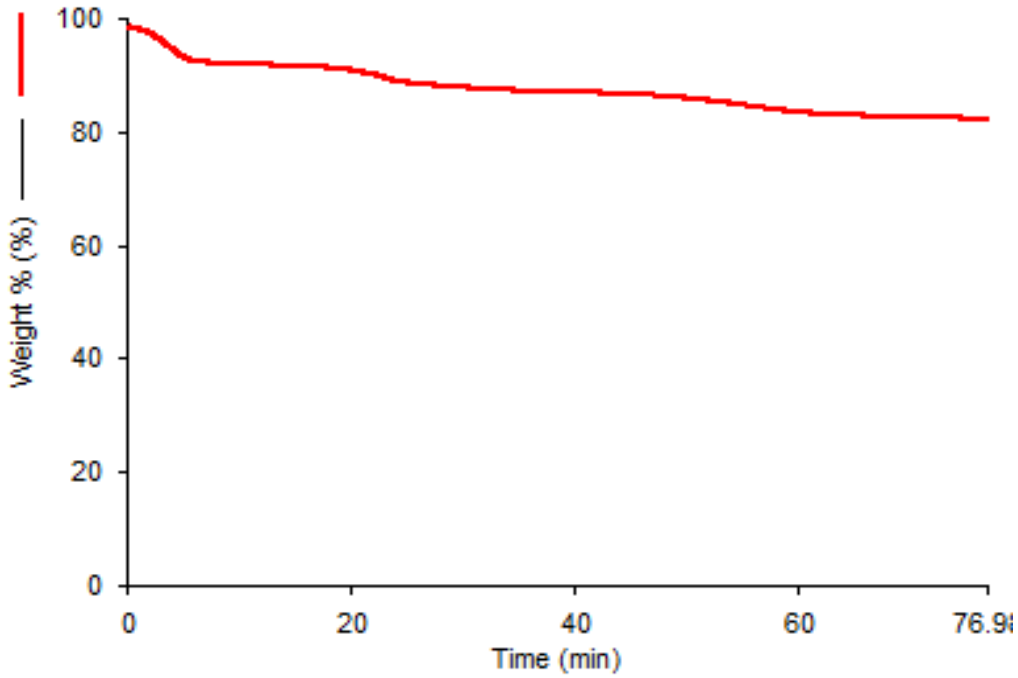


FIGURE A2.3 TGA rate of weight decomposition over time for Ni-Mg

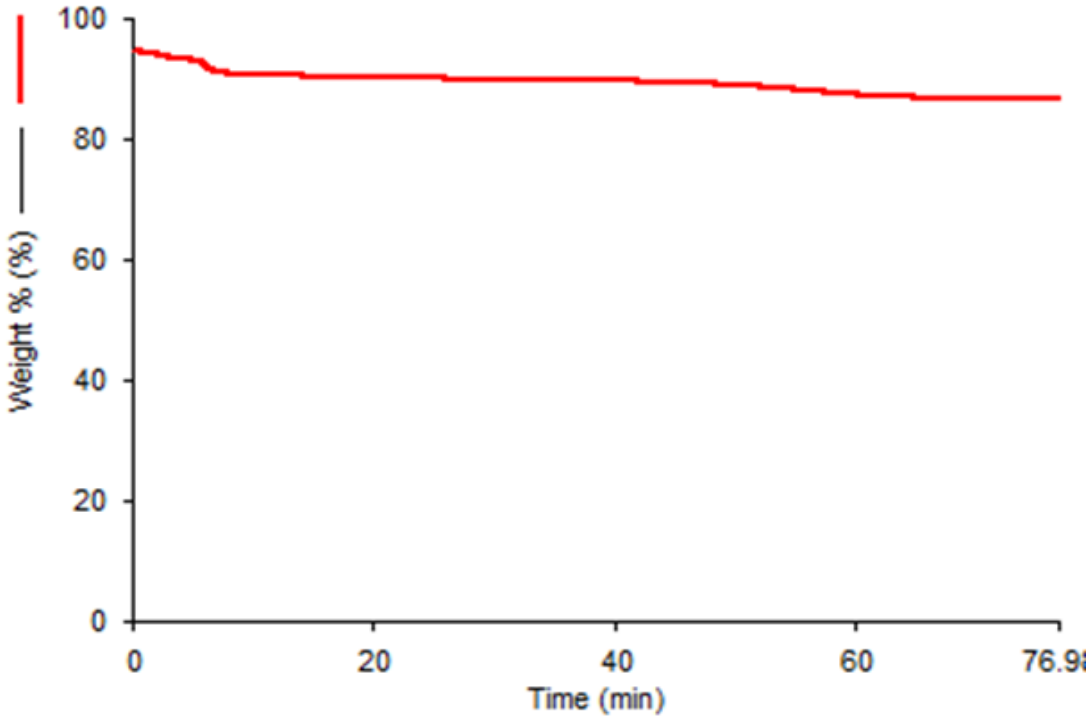


FIGURE A2.4 TGA rate of weight decomposition over time for Ni-Ce

IV EDS Distributions of Elements

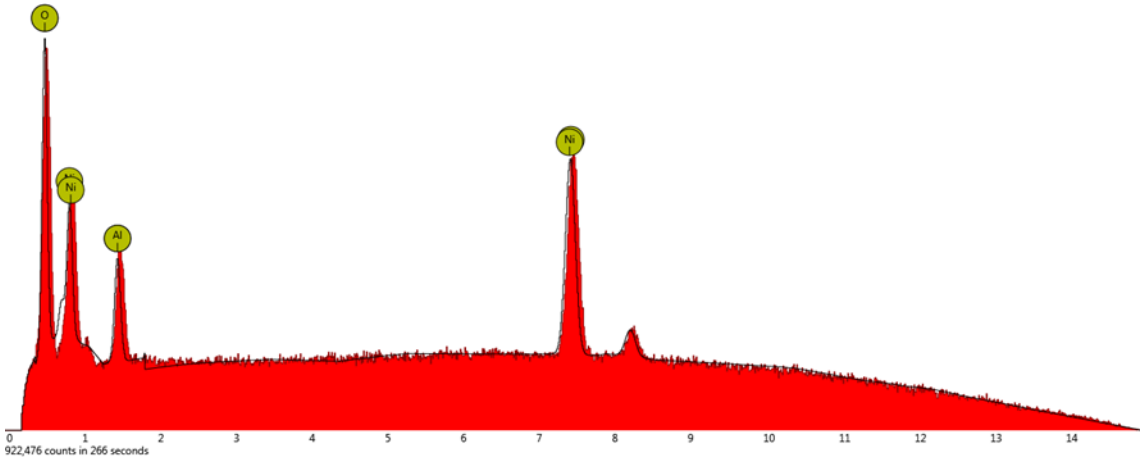


FIGURE A2.5 EDS distribution of Elements for Ni-Al

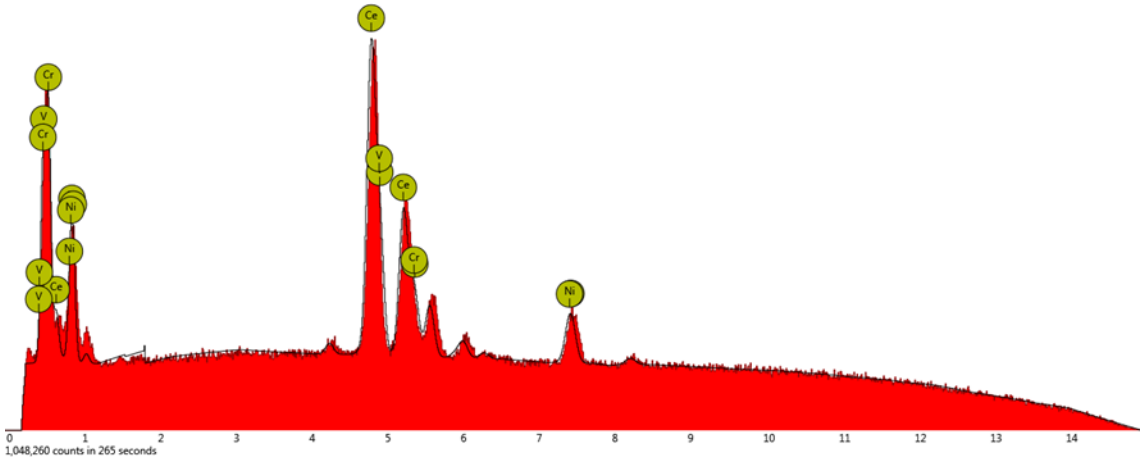


FIGURE A2.6 EDS distribution of Elements for Ni-Ce

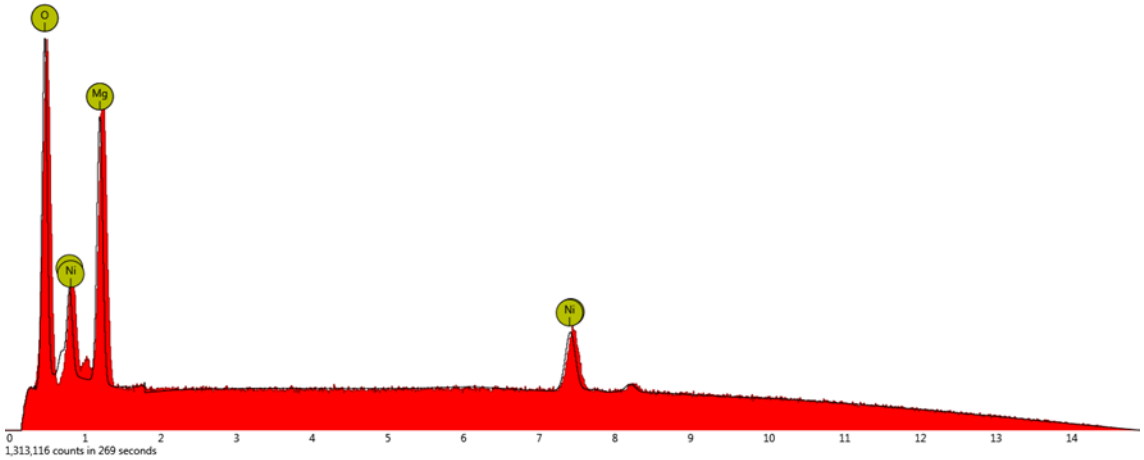


FIGURE A2.7 EDS distribution of Elements for Ni-Mg

FIGURE A2.8 Catalyst after Calcination